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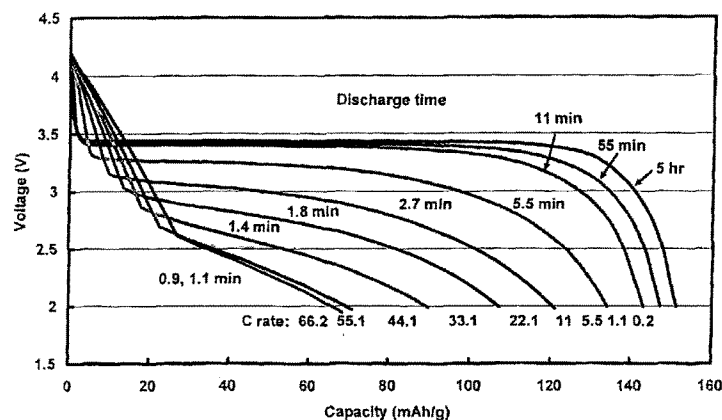
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- (71) Applicant: MASSACHUSETTS INSTITUTE OF TECHNOLOGY [US/US]; 77 Massachusetts Avenue, Cambridge, MA 02139 (US).
- (74) Agent: WALAT, Robert, H.; Wolf, Greenfield & Sacks, P.C., 600 Atlantic Avenue, Boston, MA 02210 (US).
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[Continued on next page]

(54) Title: CONDUCTIVE LITHIUM STORAGE ELECTRODE



(57) Abstract: A compound comprising a composition $A.(M'_{1-a}M''_a)_y(XD_4)_z$, $A.(M'_{1-a}M''_a)_y(DXD_4)_z$, or $A_x.(M'_{1-a}M''_a)_y(X_2D_7)_z$, and have values such that x , plus $y(1-a)$ times a formal valence or valences of M' , plus ya times a formal valence or valence of M'' , is equal to z times a formal valence of the XD_4 , X_2D_7 , or DXD_4 group; or a compound comprising a composition $(A_{1-a}M''_a)_xM'_y(XD_4)_z$, $(A_{1-a}M''_a)_xM'_y(DXD_4)_z$, $(A_{1-a}M''_a)_xM'_y(X_2D_7)_z$ and have values such that $(1-a)x$ plus the quantity ax times the formal valence or valences of M'' plus y times the formal valence or valences of M' is equal to z times the formal valence of the XD_4 , X_2D_7 or DXD_4 group. In the compound, A is at least one of an alkali metal and hydrogen, M' is a first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, molybdenum, and tungsten, M'' any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least one of oxygen, nitrogen, carbon, or a halogen, $0.0001 < a \leq 0.1$, and x , y , and z are greater than zero. The compound can have a conductivity at 27° C of at least about 10^{-8} S/cm. The compound can be a doped lithium phosphate that can intercalate lithium or hydrogen. The compound can be used in an electrochemical device including electrodes and storage batteries and can have a gravimetric capacity of at least about 80 mAh/g while being charged/discharged at greater than about C rate of the compound.

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CONDUCTIVE LITHIUM STORAGE ELECTRODE

RELATED APPLICATIONS

This application claims priority under 35 U.S.C. § 119(e) to U.S. Provisional
5 Application Serial No. 60/343,060, filed on December 21, 2001, U.S. Provisional
Application Serial No. 60/388,721, filed on June 14, 2002, and U.S. Provisional
Application Serial No. 60/412,656, filed on September 20, 2002, the disclosures of
which are herein incorporated by reference.

10

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is directed to transition metal polyanion oxides that can be
used as alkali ion combined materials and more particularly to lithium-ion intercalating
15 structures that can be used as electrochemical compounds.

2. Description of the Related Art

The published literature contains many references by those skilled in the art to the
insulating nature of these compounds, and the limitations on their utility as battery
20 storage materials thereby created. For example, Gaubicher et al. (J. Gaubicher, T. Le
Mercier, Y. Chabre, J. Angenault, and M. Quarton, "Li/β-VOPO₄: A New 4 V System
for Lithium Batteries," *J. Electrochem. Soc.*, 146[12] 4375-4379 (1999)) comment with
respect to the NASICON compounds that "unfortunately, the anionic units tend to isolate
the transition elements, which consequently leads to low electronic conductivity."

25 In "Approaching Theoretical Capacity of LiFePO₄ at Room Temperature at High
Rates," H. Huang, S.-C. Yin and L.F. Nazar, *Electrochem. Sol. St. Lett.*, 4[10] A170-
A172 (2001), explain that "however, owing to their very poor conductivity, initial reports
indicated that Li⁺ can only be partially extracted/inserted at room temperature at modest
rates." And, in "Issues and challenges facing rechargeable lithium batteries," J.-M.
30 Tarascon and M. Armand, *Nature*, 414, 359-367 (2001), note that with respect to these
compounds that "one of the main drawbacks with using these materials is their poor
electronic conductivity, and this limitation had to be overcome through various materials

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processing approaches, including the use of carbon coatings, mechanical grinding or mixing, and low-temperature synthesis routes to obtain tailored particles.”

Proposed solutions to the poor electronic conductivity have typically focused entirely on coating with carbon or adding a significant excess of carbon during synthesis.

- 5 Coating with carbon has been described by N. Ravet et al. in “Improved iron-based cathode materials,” Abstr. No. 12, ECS Fall meeting, Hawaii, 1999 and by Morcrette et al. in M. Morcrette, C. Wurm, J. Gaubicher, and C. Masquelier, “Polyanionic structures as alternative materials for lithium batteries,” Abstr. No. 93, Li Battery Discussion Meeting, Bordeaux, Archachon, 27 May – 1 June 2001. Co-synthesizing with carbon
- 10 has been discussed by H. Huang et al. at the Univ. of Waterloo and by Yamada et al. at the Electrochemical Society Fall Meeting, San Francisco, CA, September 2001. However, the addition of carbon as a conductive additive can lower the gravimetric and volumetric capacity of the storage material. In some instances, about 20 wt% carbon is added to the electrode formulation (approximately 30% by volume). This significant
- 15 volume of carbon does not typically store lithium storage at the potentials at which the polyanion compounds store lithium.

It is therefore clear and widely acknowledged by those skilled in the art that poor electronic conductivity is, firstly, an inherent feature of the lithium-metal-polyanion compounds discussed herein, and secondly, that this inherent feature limits the

20 applicability of the materials in lithium storage applications, including lithium battery electrodes, especially at temperatures near room temperature. While published literature and patents describe the addition of various metal additives to such compounds, they are silent as to whether the critical and enabling property of improved electronic conductivity can be obtained.

25

SUMMARY OF THE INVENTION

The invention provides compounds, methods of forming compounds, electrodes that comprise compounds and storage battery cells that include an electrode that comprises a compound.

- 30 In one set of embodiments, a compound is provided. The compound comprises a composition $A_x(M'_{1-a}M''_a)_y(XD_4)_z$, $A_x(M'_{1-a}M''_a)_y(DXD_4)_z$, or $A_x(M'_{1-a}M''_a)_y(X_2D_7)_z$, wherein A is at least one of an alkali metal or hydrogen, M' is a first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, boron, aluminum, silicon,

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vanadium, molybdenum and tungsten, M'' is any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least one of oxygen, nitrogen, carbon, or a halogen, $0.0001 < a \leq 0.1$, and x is equal to or greater than 0, y and z are greater than 0 and have values such that x, plus y(1-a) times a formal valence or valences of M' , plus ya times a formal valence or valence of M'' , is equal to z times a formal valence of the XD_4 , X_2D_7 , or DXD_4 group. In some of these embodiments, the compound has a conductivity at 27° C of at least about 10^{-8} S/cm. In some of these embodiments, the compound has a specific surface area of at least 15 m²/g. In some of these embodiments, the compound crystallizes in an ordered or partially disordered structure of the olivine (A_xMXO_4), NASICON ($A_x(M',M'')_2(XO_4)_3$), VOPO₄, LiFe(P₂O₇) or Fe₄(P₂O₇)₃ structure-types, and has a molar concentration of the metals ($M' + M''$) relative to the concentration of the elements X that exceeds the ideal stoichiometric ratio y/z of the prototype compounds by at least 0.0001.

In another set of embodiments, a compound is provided. The compound comprises a composition $(A_{1-a}M''_a)_xM'_y(XD_4)_z$, $(A_{1-a}M''_a)_xM'_y(DXD_4)_z$, or $(A_{1-a}M''_a)_xM'_y(X_2D_7)_z$, wherein A is at least one of an alkali metal or hydrogen, M' is a first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, boron, aluminum, silicon, vanadium, molybdenum and tungsten, M'' any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least one of oxygen, nitrogen, carbon, or a halogen, $0.0001 < a \leq 0.1$, and x, y, and z are greater than zero and have values such that (1-a)x plus the quantity ax times the formal valence or valences of M'' plus y times the formal valence or valences of M' is equal to z times the formal valence of the XD_4 , X_2D_7 or DXD_4 group. In some of these embodiments, the compound has a conductivity at 27° C of at least about 10^{-8} S/cm. In some of these embodiments, the compound has a specific surface area of at least 15 m²/g. In some of these embodiments, the compound crystallizes in an ordered or partially disordered structure of the olivine (A_xMXO_4), NASICON ($A_x(M',M'')_2(XO_4)_3$), VOPO₄, LiFe(P₂O₇) or Fe₄(P₂O₇)₃ structure-types, and has a molar concentration of the metals ($M' + M''$) relative to the concentration of the elements X that exceeds the ideal stoichiometric ratio y/z of the prototype compounds by at least 0.0001.

In another embodiment, a compound is provided. The compound comprises a composition $(A_{b-a}M''_a)_xM'_y(XD_4)_z$, $(A_{b-a}M''_a)_xM'_y(DXD_4)_z$, or $(A_{b-a}M''_a)_xM'_y(X_2D_7)_z$, wherein A is at least one of an alkali metal or hydrogen, M' is a first-row transition

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metal, X is at least one of phosphorus, sulfur, arsenic, boron, aluminum, silicon, vanadium, molybdenum and tungsten, M'' any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least one of oxygen, nitrogen, carbon, or a halogen, $0.0001 < a \leq 0.1$, $a \leq b \leq 1$, and x, y, and z are greater than zero and have values such that (b-a)x plus the quantity ax times the formal valence or valences of M'' plus y times the formal valence or valences of M' is equal to z times the formal valence of the XD₄, X₂D₇ or DXD₄ group. In some of these embodiments, the compound has a conductivity at 27° C of at least about 10⁻⁸ S/cm. In some of these embodiments, the compound has a specific surface area of at least 15 m²/g. In some of these embodiments, the compound crystallizes in an ordered or partially disordered structure of the olivine (A_xMXO₄), NASICON (A_x(M', M'')₂(XO₄)₃), VOPO₄, LiFe(P₂O₇) or Fe₄(P₂O₇)₃ structure-types, and has a molar concentration of the metals (M' + M'') relative to the concentration of the elements X that exceeds the ideal stoichiometric ratio y/z of the prototype compounds by at least 0.0001.

In another set of embodiments, methods of forming a compound are provided. The methods include mixing an alkali metal or hydrogen salt, a first-row transition metal salt, a salt of at least one of phosphorus, sulfur, arsenic, silicon, aluminum, boron, vanadium, molybdenum and tungsten, and a salt of any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal; milling the mixture; and heat treating the mixture at a temperature between 300-900°C.

In another set of embodiments, methods of doping a material to form a lithium or hydrogen storage compound are provided. The methods include selecting a starting material to be doped, in conjunction with selection of milling equipment comprising a dopant for doping the starting material at a predetermined level of dopant. The methods further include milling the starting material in the milling equipment; and recovering from the milling step a material suitable for forming a lithium or hydrogen storage compound comprising the starting material doped with the dopant at the predetermined level.

In another set of embodiments, an electrode comprising a lithium storage compound is provided. The electrode can comprise any of the compounds described above and has a material energy density (i.e., voltage vs. Li x charge capacity) that while: charging or discharging at a rate ≥ 30 mA per g of storage compound, is greater

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than 350 Wh/kg; or, charging or discharging at a rate ≥ 150 mA per g of storage compound, is greater than 280 Wh/kg; or, charging or discharging at a rate ≥ 300 mA per g of storage compound, is greater than 270 Wh/kg; or, charging or discharging at a rate ≥ 750 mA per g of storage compound, is greater than 250 Wh/kg; or, charging or
5 discharging at a rate ≥ 1.5 A per g of storage compound, is greater than 180 Wh/kg; or, charging or discharging at a rate ≥ 3 A per g of storage compound, is greater than 40 Wh/kg; or, charging or discharging at a rate ≥ 4.5 A per g of storage compound, is greater than 10 Wh/kg.

In another set of embodiments, an electrode comprising a lithium storage
10 compound is provided. The lithium storage compound is a compound other than one of ordered or partially ordered rocksalt crystal structure type, or spinel crystal structure type, or vanadium oxide or manganese oxide. The compound has a material energy density (i.e., voltage vs. Li x charge capacity) that while: charging or discharging at a rate ≥ 800 mA per g of storage compound, is greater than 250 Wh/kg; or, charging or
15 discharging at a rate ≥ 1.5 A per g of storage compound, is greater than 180 Wh/kg; or, charging or discharging at a rate ≥ 3 A per g of storage compound, is greater than 40 Wh/kg; or, charging or discharging at a rate ≥ 4.5 A per g of storage compound, is greater than 10 Wh/kg.

In another set of embodiments, an electrode is provided. The electrodes includes
20 a current collector comprising any of the compounds described above.

In another set of embodiments, a storage battery cell is provided. The storage battery comprises a positive electrode, a negative electrode and a separator positioned between the positive electrode and the negative electrode. At least one of the positive electrode or negative electrode comprises any of the compounds described above.

25 Other embodiments and novel features of the invention should become apparent from the following detailed description when considered in conjunction with the accompanying drawings. In cases of conflict between an incorporated reference and the present specification, the present specification shall control.

30 BRIEF DESCRIPTION OF DRAWINGS

Preferred, non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying drawings, in which:

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FIG. 1 is a copy of an TEM image of a compound with 0.1% Ti doping, prepared according to the method substantially described in Example 1 and heat treated at 600° C in argon for twenty-four hours, showing that the primary crystallite size is about 100 - 200 nm and that the primary crystallites are aggregated into larger particles; and showing
5 that there is no surface coating or other continuous phase which could provide improved electronic conductivity; thus, the improved electronic conductivity is likely due to an improvement in the compound itself;

FIG. 2 are copies of scanning transmission electron microscope images and energy-dispersive x-ray composition maps of a 1% Ti-doped sample prepared according
10 to the method substantially described in Example 1 and heat treated at 600° C in nitrogen for twenty-four hours or 800° C in argon for sixteen hours. In the sample heat treated at 600° C, there is detectable Ti in solid solution in the compound as well as an excess of Ti appearing as an additional phase whereas the sample heat treated at 800° C shows no Ti detectable in the phase itself, thus showing that the solid solubility of Ti under these
15 conditions is likely less than about 0.1%;

FIG. 3 are copies of scanning transmission electron microscope images and energy-dispersive x-ray composition maps of an 0.2% Nb-doped sample prepared according to the method substantially described in Example 1 and heat treated at 600° C for twenty-four hours, 700° C for twenty hours, and 800° C for fifteen hours, all in argon,
20 showing that in the sample heat treated at 600° C, substantial amounts of Nb can be detected within the LiFePO₄ grains and a Nb-rich additional phase is substantially absent; in the samples heat treated at 700° C and 800° C, substantially less Nb is detectable in the grains and Nb-rich additional phase has appeared, and thus showing that the solubility of Nb is at least about 0.2% when the material is prepared according to
25 Example 1 and heat treated at 600° C, whereas heat treating at a temperature of 700° C, or greater, causes exsolution of Nb;

FIG. 4 is a graph showing x-ray diffraction patterns of materials prepared according to Example 1, undoped samples and samples containing 1% Ti, 1% Zr, 2% Ti, and 2% Zr, heat treated at 600° C in nitrogen for twenty-four hours, showing that
30 additional phases can be detectable in all of the doped samples and thus that, the solubility limit of the dopants is less than 1% under these preparation conditions; the composition heat treated in argon and nitrogen being substantially similar to that shown

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in FIG. 15; thus showing that multiple non-oxidizing gas atmospheres can be used to prepare the electronically conductive materials of the invention;

FIG. 5 is a copy of TEM images of a powder of nominal composition $\text{LiFe}_{0.99}\text{Zr}_{0.01}\text{PO}_4$ and prepared according to the Example 1, showing crystalline particles
5 in which lattice fringes are visible and which do not possess a distinguishable surface phase of another material such as carbon;

FIG. 6A and 6B show X-ray diffraction patterns of various powders showing the effect of cation stoichiometry on dopant solid-solubility. FIG. 35A shows powders containing 1 atom% dopant in the stoichiometry $\text{Li}_{1-x}\text{M}_x\text{FePO}_4$ are single-phase by XRD
10 and TEM/STEM analysis. FIG. 35B shows powders containing 1 atom% dopant in the stoichiometry $\text{LiFe}_{1-x}\text{M}_x\text{PO}_4$ show Li_3PO_4 precipitation by XRD, and secondary phases enriched in the dopant by TEM/STEM (not shown);

FIGS. 7A-7D show elemental maps obtained by STEM of a powder of composition $\text{Li}_{0.99}\text{Nb}_{0.01}\text{FePO}_4$ (fired 600°C , 20 h, in argon) which illustrate the uniform
15 dopant solid solution observed in compositions of stoichiometry $\text{Li}_{1-x}\text{M}_x\text{FePO}_4$;

FIGS. 8 and 9 are graphs showing the conductivity of doped and undoped samples as a function of temperature;

FIG. 10 shows backscattered electron images of the polished cross-section of two Nb-doped and one undoped pellet sintered to high density;

FIG. 11 is the configuration of a four-point microcontact measurement performed
20 to determine the electronic conductivity of samples;

FIG. 12 is the electrical conductivity measured at several locations within each of the three samples of FIG. 10;

FIG. 13 shows bright-field TEM images of powders of 1% Nb and 1% Zr doping
25 level and prepared according to the invention;

FIG. 14 shows a TEM image of a conductive 1% Nb doped composition fired at 600°C , showing a particle of incompletely reacted precursor and crystallized olivine phase, and energy-dispersive X-ray spectra taken with a focused electron probe at the locations indicated, showing that carbon is enriched within the particle of unreacted
30 precursor and not detected within several locations of the olivine phase;

FIGS. 15 and 16 show high resolution TEM images of a conductive 1% Nb doped composition fired at 600°C , in which lattice fringes are visible in crystallites of

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olivine phase, and showing the absence of a significant surface coating of another material;

FIG. 17A shows a first electrochemical cycle for an electrode prepared using a Nb-doped composition, and tested against a lithium metal negative electrode in a laboratory cell using a nonaqueous liquid electrolyte. FIG. 17B shows capacity vs. cycle number for this electrode at a 1C rate (150 mA/g). FIG. 17C shows the coulombic efficiency vs. cycle number at 1C rate (150 mA/g);

FIGS. 18A and 18B show electrochemical test data for electronically conductive olivine of composition $\text{Li}_{0.99}\text{Zr}_{0.01}\text{FePO}_4$ s in a conventional lithium battery electrode design (78 wt% cathode-active material, 10 wt% Super P™ carbon, 12 wt% PVdF binder; 2.5 mg/cm² loading) with a lithium metal negative electrode and nonaqueous liquid electrolyte. FIG. 18A shows results of cycle testing which indicates high and stable reversible capacity for more than 150 cycles at a variety of current rates. Significant capacity with high coulombic efficiency (>99.5%) is retained at rates as high as 3225 mA/g (21.5C). FIG. 18B shows charge-discharge curves indicating little polarization even at the highest current rates, attributed to the high electronic conductivity and high specific surface area of the olivine powder;

FIG. 19 shows discharge curves for continuous cycling between 2-4.2V for an electrode made using $\text{Li}_{0.99}\text{Zr}_{0.01}\text{FePO}_4$ powder and tested to discharge rates of 66.2C (9.93 A/g) at a temperature of 42°C in a conventional cell design using a lithium metal negative electrode and nonaqueous liquid electrolyte;

FIG. 20 shows discharge curves for constant-current constant-voltage cycling between 2-3.8V for an electrode made using $\text{Li}_{0.99}\text{Zr}_{0.01}\text{FePO}_4$ powder and tested to discharge rates of 200C (30 A/g) at a temperature of 22°C in a conventional cell design using a lithium metal negative electrode and nonaqueous liquid electrolyte;

FIG. 21 shows discharge capacity vs. discharge rate curves for several electrodes formulated using $\text{Li}_{0.99}\text{Zr}_{0.01}\text{FePO}_4$ powder heat treated at 600°C or 700°C, and tested to high discharge rates greater than 60C (9 A/g) at 22-23°C in a conventional cell design using a lithium metal negative electrode and nonaqueous liquid electrolyte;

FIG. 22 shows discharge capacity vs. discharge rate curves for two electrodes formulated using undoped LiFePO_4 powder heat treated at 700°C, and tested at 23°C in a

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conventional cell design using a lithium metal negative electrode and nonaqueous liquid electrolyte;

FIG. 23 shows discharge capacity vs. discharge rate curves for several LiFePO₄ electrodes described in published literature, compared to an electrode of the invention containing Li_{0.99}Zr_{0.01}FePO₄ powder, showing the markedly higher discharge capacity available at high discharge rates of the electrodes of the invention;

FIG. 24 shows the discharge energy density in mAh/g vs. the current density in mA/g for an electrode formulated using Li_{0.99}Zr_{0.01}FePO₄ powder and measured at a temperature of 22°C;

FIG. 25 shows the discharge energy density in mAh/g vs. the current density in mA/g for an electrode formulated using Li_{0.99}Zr_{0.01}FePO₄ powder and measured at temperatures of 23, 31, and 42°C;

FIG. 26 shows the discharge energy density in mAh/g vs. the current density in mA/g for an electrode formulated using Li(Fe_{0.98}Ti_{0.02})PO₄ powder and measured at 23°C;

FIG. 27 shows the discharge energy density in mAh/g vs. the current density in mA/g for an electrode formulated using undoped LiFePO₄ and measured at temperatures of 23, 31, and 42°C.

FIG. 28 shows a Ragone plot of log power density vs. log energy density for storage battery cells based on the lithium storage materials and electrodes of the invention, compared with other storage battery technology, showing the improved power density that is available while still having high energy density.

FIG. 29 shows a schematic storage battery cell according to one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

LiFePO₄ and Li(Mn,Fe)PO₄ are ordered olivine structure compounds also known as the mineral triphylite. They belong to the general group known as polyanion compounds with tetrahedral "anion" structural units (XO₄)ⁿ, along with oxygen octahedra occupied by a transition metal M, and can include compounds of Li_xMXO₄ (olivine), Li_xM₂(XO₄)₃ (NASICON), VOPO₄, LiFe(P₂O₇) or Fe₄(P₂O₇)₃ structure, and structures related to these by having additional metal ions occupying interstitial sites,

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symmetry-changing displacements, or minor changes in the connectivity of polyhedra. Here, X is comprised of a metal that can occupy tetrahedral sites within the polyanion groups and has a significant covalent bonding character. X can be P, S, As, Mo, W, Al, Si, or B. According to the present invention, these compounds can be used as lithium
5 storage electrode materials because of their high lithium-insertion potential (relative to lithium metal), high theoretical capacity, low cost, ease of synthesis, and stability when used with common organic electrolyte systems. Despite these characteristics, it has been widely recognized that one of the limitations of this series of compounds is their low electronic conductivity, which greatly limits the practicality of these materials in battery
10 systems. Related compounds such as $(\text{Mg,Fe})\text{SiO}_4$ are also electronic insulators at an near room temperature, and only have appreciable electronic conductivity at greatly elevated temperatures.

It is therefore a surprising and unexpected discovery that certain compositions of LiFePO_4 , prepared from starting materials of lithium salts, iron compounds, and
15 phosphorous salts, including but not limited to, lithium carbonate, ammonium phosphate, and iron oxalate, and to which a low additional concentration of a metal supervalent to Li, such as, but not limited to, Mg, Al, Ti, Fe, Mn, Zr, Nb, Ta, and W, such as in the form of a metal oxide or metal alkoxide, have been added, and which is heat treated (HT) at a certain temperature range and atmosphere, exhibit increased electronic conductivity
20 at and near room temperature to render the compounds useful as lithium storage materials.

As used herein, the electrical conductivity of materials will be given in units of S/cm, electrical resistivity in units of ohm-cm ($\Omega\text{-cm}$), resistance in ohms (Ω), charge and discharge capacity in units of ampere hours per kilogram of the storage material
25 (Ah/kg) or milliamper hour per gram of storage material (mAh/g), charge and discharge rate in units of both milliamperes per gram of the storage compound (mA/g), and C rate. When given in units of C rate, the C rate is defined as the inverse of the time, in hours, necessary to utilize the full capacity of the battery measured at a slow rate. A rate of 1C refers to a time of one hour; a rate of 2C refers to a time of half an hour, a rate of C/2
30 refers to a time of two hours, and so forth. Typically, the C rate is computed from the rate, in mA/g, relative to the capacity of the compound or battery measured at a lower rate of C/5 or less. For example, in some examples herein the nominal capacity of a doped LiFePO_4 compound at low rate is about 150 mAh/g, and therefore a rate of 1C

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corresponds to a current rate of 150 mA/g, a rate of C/5 corresponds to 30 mA/g, a rate of 5C corresponds to 750 mA/g, and so forth.

In one aspect, the present invention is directed to increasing the electronic conductivity of transition metal polyanion compounds so that they can be used as alkali ion storage materials, for example, rechargeable lithium ion batteries. The compounds of the invention have electronic conductivities near room temperature, for example at a temperature of 22°C-27°C, of at least about 10^{-8} S/cm. However, in some cases, the conductivity is at least about at least about 10^{-7} S/cm, in other cases, at least about 10^{-6} S/cm, in yet other cases, at least about 10^{-5} S/cm, in still other cases, at least about 10^{-4} S/cm, in preferred cases, at least about 10^{-3} S/cm, and in more preferred cases, at least about 10^{-2} S/cm. Where elements and groups in the Periodic Table are referred to, the Periodic Table catalog number S-18806, published by the Sargent-Welch company in 1994, is used as a reference.

In one aspect, the present invention is directed to increasing the electronic conductivity of transition metal polyanion compounds so that they can be used as alkali ion storage materials, for example, rechargeable lithium ion batteries, without adding excessive amounts of an additional conductive compound such as carbon. Accordingly, the present invention can include conductivity-enhancing additives, such as but not limited to conductive carbon black, at, for example, less than about 15 weight percent, or in some cases, less than about 10 weight percent, in other cases, less than about 7 weight percent, in other cases, less than 3 weight percent, in other cases, less than 1 weight percent and, in some cases, no conductivity-enhancing additive.

In another aspect, the present invention is directed to decreasing the particle or crystallite size, or increasing the specific surface area (typically given in square meters per gram of the material, m^2/g , and measured by such methods as the Brunauer-Emmett-Teller (BET) gas adsorption method) of transition metal polyanion compounds in order to provide improved electrochemical energy storage, including improved charge storage capacity, improved energy density and power density when used in an electrochemical cell, and improved cycle life when the electrochemical cell is reversibly charged and discharged. Compositions are provided for compounds of high specific surface area, including those that are substantially fully crystallized, or those that have substantial electronic conductivity. The materials of the invention have specific surface areas of at

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least 15 m²/g. However, in other cases they have specific surface areas of at least 20 m²/g, in other cases at least 30 m²/g, and in other cases at least 40 m²/g.

In another aspect, the present invention provides methods for preparing the transition metal polyanion compounds of the invention, including compounds with
5 substantial electronic conductivity and/or high specific surface area and small particle or crystallite size.

In another aspect, the invention comprises storage electrodes, including those using the transition metal polyanion compounds of the invention. Such storage electrodes have useful properties for electrochemical energy storage including having
10 high storage energy density, high power density, and long cycle life when used reversibly in an electrochemical device. Formulations of and methods for preparing said electrodes are provided.

In another aspect, the invention comprises storage battery cells, including those using the transition metal polyanion compounds of the invention. Such cells have useful
15 energy storage characteristics including high energy density and high power density, and long cycle life.

Electronic Conductivity

In one embodiment, the present invention provides an electrochemical device
20 comprising an electrode comprising a compound with a formula $\text{Li}_x\text{Fe}_{1-a}\text{M}^n_a\text{PO}_4$, and a conductivity at 27°C, of at least about 10⁻⁸ S/cm. However, in some cases, the conductivity is at least about at least about 10⁻⁷ S/cm, in other cases, at least about 10⁻⁶ S/cm, in yet other cases, at least about 10⁻⁵ S/cm, in still other cases, at least about 10⁻⁴ S/cm, in preferred cases, at least about 10⁻³ S/cm, and in more preferred cases, at least
25 about 10⁻² S/cm.

In another embodiment, the present invention provides an electrochemical device comprising an electrode comprising a compound with a formula $\text{Li}_x\text{Fe}_{1-a}\text{M}^n_a\text{PO}_4$, the compound having a gravimetric capacity of at least about 80 mAh/g while the device is charging/discharging at greater than about C rate. However, in some embodiments, the
30 capacity is at least about 100 mAh/g, or in other embodiments, at least about 120 mAh/g, in preferred embodiments, at least about 150 mAh/g, and in still other embodiments, at least about 160 mAh/g. The present invention can, in some embodiments, also provide a capacity up to the theoretical gravimetric capacity of the compound.

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In another embodiment, the present invention provides an electrochemical device comprising an electrode comprising a compound with a formula $\text{Li}_{x-a}\text{M}''_a\text{FePO}_4$.

In another embodiment, the present invention provides an electrochemical device comprising an electrode comprising a compound with a formula $\text{Li}_{x-a}\text{M}''_a\text{FePO}_4$, and a
 5 conductivity at 27° C of at least about 10^{-8} S/cm. However, in some cases, the conductivity is at least about at least about 10^{-7} S/cm, in other cases, at least about 10^{-6} S/cm, in yet other cases, at least about 10^{-5} S/cm, in still other cases, at least about 10^{-4} S/cm, and in preferred cases, at least about 10^{-3} S/cm, and in more preferred cases, at least about 10^{-2} S/cm.

10 In another embodiment, the present invention provides an electrochemical device comprising an electrode comprising a compound with a formula $\text{Li}_{x-a}\text{M}''_a\text{FePO}_4$, the compound having a gravimetric capacity of at least about 80 mAh/g while the device is charging/discharging at greater than about C rate. However, in some embodiments, the capacity is at least about 100 mAh/g, or in other embodiments, at least about 120 mAh/g,
 15 in preferred embodiments, at least about 150 mAh/g and in still other preferred embodiments, at least about 170 mAh/g. The present invention can, in some embodiments, also provide a capacity up to the theoretical gravimetric capacity of the compound.

According to one embodiment, a composition comprising a compound with a
 20 formula $\text{A}_x(\text{M}'_{1-a}\text{M}''_a)_y(\text{XD}_4)_z$, $\text{A}_x(\text{M}'_{1-a}\text{M}''_a)_y(\text{DXD}_4)_z$ or $\text{A}_x(\text{M}'_{1-a}\text{M}''_a)_y(\text{X}_2\text{D}_7)_z$, has a conductivity at about 27° C of at least about 10^{-8} S/cm, wherein A is at least one of an alkali metal and hydrogen, M' is a first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, molybdenum and tungsten, M'' is any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least one of
 25 oxygen, nitrogen, carbon, or a halogen, $0.0001 < a \leq 0.1$, and x, y, and z have values such that x plus the quantity $y(1-a)$ times a formal valence or valences of M', plus the quantity ya times a formal valence or valence of M'', is equal to z times a formal valence of the XD_4 , X_2D_7 , or DXD_4 group. x, y, and z are typically greater than 0. The conductivity of the compound can be at least about 10^{-5} S/cm, at least about 10^{-4} S/cm, and, in some
 30 cases, at least about 10^{-2} S/cm. In some embodiments, A is lithium and $x/(x+y+z)$ can range from about zero to about one third, or about zero to about two thirds. In one embodiment, X is phosphorus, while in other embodiments, M' is iron. M'' can be any of aluminum, titanium, zirconium, niobium, tantalum, tungsten, or magnesium. M'' can

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be substantially in solid solution in the crystal structure of the compound. Typically, the compound has at least one of an olivine, NASICON, VOPO_4 , $\text{LiFe}(\text{P}_2\text{O}_7)$ or $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ structure, or mixtures thereof.

In some embodiments, the compound is LiFePO_4 .

5 In some embodiments, M'' is at least partially in solid solution in the crystal structure of the compound at a concentration of at least 0.01 mole % relative to the concentration of M' , the balance appearing as an additional phase, at least 0.02 mole % relative to the concentration of M' , the balance appearing as an additional phase, and in yet other embodiments, at least 0.05 mole % relative to the concentration of M' , the
10 balance appearing as an additional phase and, in still other embodiments, at a concentration of at least 0.1 mole % relative to the concentration of M' , the balance appearing as an additional phase.

In some embodiments, the compound can be formed as particles or crystallites wherein at least 50% of which have a smallest dimension that is less than about 500 nm.
15 However, in some cases, the smallest dimension is less than 200 nm, in yet other cases, the smallest dimension is less than 100 nm, in still other cases, the smallest dimension is less than 50 nm, in still other cases, the smallest dimension is less than 20 nm, and in still other cases, the smallest dimension is less than 10 nm. In some embodiments, the compound forms an interconnected porous network comprising crystallites with a
20 specific surface area of at least about $10 \text{ m}^2/\text{g}$. However, in some cases, the specific surface area is at least about $20 \text{ m}^2/\text{g}$, in other cases, the specific surface area is at least about $30 \text{ m}^2/\text{g}$, in other cases, the specific surface area is at least about $40 \text{ m}^2/\text{g}$, in other cases, the specific surface area is at least about $50 \text{ m}^2/\text{g}$. Smallest dimension, in this context, means a cross-section.

25 In some cases, the present invention provides a compound with a formula $(\text{A}_{1-a}\text{M}''_a)_x\text{M}'_y(\text{XD}_4)_z$, $(\text{A}_{1-a}\text{M}''_a)_x\text{M}'_y(\text{DXD}_4)_z$, or $(\text{A}_{1-a}\text{M}''_a)_x\text{M}'_y(\text{X}_2\text{D}_7)_z$ that has a conductivity at 27°C of at least about 10^{-8} S/cm , wherein A is at least one of an alkali metal and hydrogen, M' is a first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, molybdenum, and tungsten, M'' any of a Group IIA, IIIA, IVA, VA, VIA,
30 VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least one of oxygen, nitrogen, carbon, or a halogen, $0.0002 < a \leq 0.1$, and x , y , and z have values such that $(1-a)x$ plus the quantity ax times the formal valence or valences of M'' plus y times the formal valence or valences of M' is equal to z times the formal valence of the XD_4 , X_2D_7

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or DXD₄ group. x , y , and z are typically greater than zero. The conductivity of the compound can be at least about 10^{-5} S/cm, at least about 10^{-4} S/cm, and, in some cases, at least about 10^{-2} S/cm. In some embodiments, A is lithium and $x/(x+y+z)$ can range from about zero to about one third. In one embodiment, X is phosphorus, while in other

5 embodiments, M' is iron. M'' can be any of aluminum, titanium, zirconium, niobium, tantalum, tungsten, or magnesium. M'' can be substantially in solid solution in the crystal structure of the compound. Typically, the compound has at least one of an olivine, NASICON, VOPO₄, LiFe(P₂O₇) or Fe₄(P₂O₇)₃ structure, or mixtures thereof. In some embodiments, the compound is LiFePO₄. In some embodiments, M'' is at least

10 partially in solid solution in the crystal structure of the compound at a concentration of at least 0.01 mole % relative to the concentration of M', the balance appearing as an additional phase, at least 0.02 mole % relative to the concentration of M', the balance appearing as an additional phase, and in yet other embodiments, at least 0.05 mole % relative to the concentration of M', the balance appearing as an additional phase and, in

15 still other embodiments, at a concentration of at least 0.1 mole % relative to the concentration of M', the balance appearing as an additional phase.

In some embodiments, the electronically conductive lithium transition metal phosphate olivine compound has a suitable electronic conductivity greater than about 10^{-8} S/cm. The electronically conductive lithium transition metal phosphate compound

20 can be a composition $\text{Li}_x(\text{M}'_{1-a}\text{M}'')_a\text{PO}_4$ or $\text{Li}_{x-a}\text{M}'_a\text{M}''\text{PO}_4$, and can crystallize in the ordered-olivine or triphylite structure, or a structure related to the ordered olivine or triphylite structure with small displacements of atoms without substantial changes in the coordination number of anions around cations, or cations around anions. In such compounds Li⁺ substantially occupies the octahedral site typically designated as M1, and

25 a substantially divalent cation M' substantially occupies the octahedrally-coordinated site typically designated as M2, as described in the olivine structure given in "Crystal Chemistry of Silicate Minerals of Geophysical Interest," by J. J. Papike and M. Cameron, *Reviews of Geophysics and Space Physics*, Vol. 14, No. 1, pages 37-80, 1976. In some embodiments, the exchange of Li and the metal M' between their respective

30 sites in a perfectly ordered olivine structure is allowed so that M' may occupy either site. M' is typically one or more of the first-row transition metals, V, Cr, Mn, Fe, Co, or Ni. M'' is typically a metal with formal valence greater than 1+ as an ion in the crystal structure.

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In some embodiments, M' , M'' , x , and a are selected such that the compound is a crystalline compound that has in solid solution charge compensating vacancy defects to preserve overall charge neutrality in the compound. In the compositions of type $Li_x(M'_{1-a}M''_a)PO_4$ or $Li_{x-a}M''_aM'PO_4$, this condition can be achieved when a times the formal valence of M'' plus $(1-a)$ times the formal valence of M' plus x is greater than 3+, necessitating an additional cation deficiency to maintain charge neutrality, such that the crystal composition is $Li_x(M'_{1-a-y}M''_a vac_y)PO_4$ or $Li_{x-a}M''_aM'_{1-y} vac_y PO_4$, where vac is a vacancy. In the language of defect chemistry, the dopant can be supervalent and can be added under conditions of temperature and oxygen activity that promote ionic compensation of the donor, resulting in nonstoichiometry. The vacancies can occupy either M1 or M2 sites. When $x < 1$, the compound also has additional cation vacancies on the M1 site in a crystalline solid solution, said vacancies being compensated by increasing the oxidation state of M'' or M' . In order to increase the electronic conductivity usefully, a suitable concentration of said cation vacancies should be greater than or equal to 10^{18} per cubic centimeter.

In some cases, the compound has an olivine structure and contains in crystalline solid solution, amongst the metals M' and M'' , simultaneously the metal ions Fe^{2+} and Fe^{3+} , Mn^{2+} and Mn^{3+} , Co^{2+} and Co^{3+} , Ni^{2+} and Ni^{3+} , V^{2+} and V^{3+} , or Cr^{2+} and Cr^{3+} , with the ion of lesser concentration being at least 10 parts per million of the sum of the two ion concentrations.

In some embodiments, the compound has an ordered olivine structure and A , M' , M'' , x , and a are selected such that there can be Li substituted onto M2 sites as an acceptor defect. In the compositions of type $Li_x(M'_{1-a}M''_a)PO_4$ or $Li_{x-a}M''_aM'PO_4$, typical corresponding crystal compositions are $Li_x(M'_{1-a-y}M''_a Li_y)PO_4$ or $Li_{x-a}M''_aM'_{1-y} Li_y PO_4$. In this instance, the subvalent Li substituted onto M2 sites for M' or M'' can act as an acceptor defect. In order to increase the electronic conductivity usefully, a suitable concentration of said Li on M2 sites should be greater than or equal to 10^{18} per cubic centimeter.

In some embodiments, the present invention provides a p-type semiconducting composition, $Li_x(M'_{1-a}M''_a)PO_4$, $Li_xM''_aM'PO_4$, $Li_x(M'_{1-a-y}M''_a vac_y)PO_4$, $Li_{x-a}M''_aM'_{1-y} vac_y PO_4$, $Li_x(M'_{1-a-y}M''_a Li_y)PO_4$ or $Li_{x-a}M''_aM'_{1-y} Li_y PO_4$. M'' is a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB element of the Periodic Table (catalog number S-18806, published by the Sargent-Welch company in

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1994.) Magnesium is an example of a dopant from Group IIA, Y is an example of a dopant from Group IIIA, Ti and Zr are examples of dopants from Group IVA, Nb and Ta are examples of dopants from Group VA, W is an example of a dopant from Group VIA, Fe is an example of a metal from Group VIIIA, and Al is an example of a dopant from
 5 Group IIIB.

x can have a value between zero and 1.1 in the initially prepared material, and during its use as an lithium ion storage compound, x can vary between about zero and about 1.1. a can have a value between about 0.0001 and 0.1. In some embodiments, out of the total amount a of M'' , at least 0.0001 is in solid solution in the crystalline structure
 10 of the compound.

In some embodiments, M' is Fe and the solubility of M'' in the lattice can be improved if M'' has an ionic radius, in octahedral coordination, that is less than that of Fe^{2+} . Achieving solid solubility sufficient to increase the electronic conductivity above 10^{-8} S/cm can require that processing conditions (for example, temperature, atmosphere,
 15 starting materials) allow M'' to be stabilized in a particular valence state that would provide an ionic radius less than that of Fe^{2+} . In some cases, for example, when solid solubility is achieved, the M'' ion may occupy the M1 site, or it may preferentially occupy the M2 site and cause Fe^{2+} or Fe^{3+} , which would normally occupy the M2 site, to occupy the M1 site.

20 Generalizing the M'' solubility requirement to other olivines of composition $Li_x M''_a M'_{1-a} PO_4$, M'' typically has an ionic radius that is less than the average ionic radius of ions M' at the Li concentration x at which the compound is first synthesized. Electrochemical insertion and removal can later change the valence distribution amongst the M' and M'' ions.

25 In some cases, M'' can be in the desired valence state and concentration by adding, to the starting material, a salt of M'' having the desired final valence. However, the desired valence distribution amongst metals M' and M'' can be obtained by synthesizing or heat treating under appropriate conditions of temperature and gas atmosphere. For example, if M' is Fe, heat treatment should be conducted under
 30 temperature and atmosphere conditions that preserve a predominantly 2+ valence state, although some Fe^{3+} is allowable and can even be beneficial for increasing conductivity.

In other cases, for example, for $Li_x (M'_{1-a} M''_a) PO_4$ compositions, firing or heat treating at 600° C, can render the compositions conductive, even if M'' , or M' , is a

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divalent cation, such as Mg^{2+} or Mn^{2+} . In some cases, a Li_3PO_4 secondary phase can be present. Thus, the olivine composition according to some embodiments of the present invention may have a lithium deficiency that can result in a $\text{Li}_{x-a}\text{M}'_a\text{M}''\text{PO}_4$ crystal composition.

5 The possible dopants M'' are not limited to those Groups of the Periodic Table that were previously identified, rather, M'' can be any metal that satisfies the above requirements of size and valence. Specifically, for compositions $\text{Li}_{x-a}\text{M}'_a\text{M}''\text{PO}_4$, where M' is Fe, M'' may be Mg^{2+} , Mn^{2+} , Fe^{3+} , Al^{3+} , Ce^{3+} , Ti^{4+} , Zr^{4+} , Hf^{4+} , Nb^{5+} , Ta^{5+} , W^{6+} , or combinations thereof.

10 In another embodiment, the compounds of this invention can be used as mixed protonic-electronic conductors for such applications as fuel cell electrodes and gas-separation membranes. Phospho-olivines, such as LiFePO_4 , can be doped to be highly electronically conducting, while at the same time they can be sufficiently lithium-ion conducting to provide good performance as a lithium battery electrode. Electrochemical
15 results show good cycling and also demonstrate that the compound can be delithiated while retaining good electronic conductivity. In some cases, the olivine structure can be retained in the fully delithiated state. That is, FePO_4 has an olivine structure-type polymorph. Therefore, a doped FePO_4 may be protonatable to be a good mixed protonic-electronic conductor, since phosphates are good protonic conductors.

20 The conductive LiMPO_4 compounds of this invention may also be protonatable to form H_xFePO_4 conductors, where $0 < x < 1.1$. Such compounds can be used as the electrode in a proton-conducting fuel cell. Typically such an electrode can be used with a proton-conducting and electronically insulating electrolyte. Such compounds can also be used as a solid membrane for separating hydrogen gas from gas mixtures. For
25 example, hydrogen can be dissociated to protons and electrons at one surface of the membrane that is under a higher hydrogen partial pressure, the protons would typically diffuse through the membrane to a second surface at lower hydrogen partial pressure, and are recombined with electrons to form hydrogen gas that would be released to the atmosphere from the second surface.

30 In some embodiments, compounds of the invention have a structure comprising a continuous network of transition-metal filled anion polyhedral units. The polyhedral units may be octahedrals or distorted octahedrals. The polyhedral units in the structure can, for example, share at least one of vertices, corners, edges, or faces with other

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changes in conductivity with further increases in dopant concentration. For compositions $\text{Li}_{1-a}\text{M}''_a\text{FePO}_4$, the electronic conductivity is firstly higher overall by at least about an order of magnitude than for any of the $\text{LiFe}_{1-a}\text{M}''_a\text{PO}_4$ compositions. Compared to the undoped material, the increase in conductivity is significant, greater by a factor of more than 10^7 times, with a doping level as low as 0.2% (Nb-doped). However, further doping increases the conductivity only modestly.

Materials were also synthesized that contained an excess of Fe, typically in the form of an Fe^{2+} or Fe^{3+} salt, as shown in Table 2. While an excess of either Fe^{2+} or Fe^{3+} can be substituted into the composition $\text{Li}_{1-a}\text{M}''_a\text{FePO}_4$, as with the other dopants M'' , a certain concentration must be in solid solution (i.e., form part of the crystal lattice) for the conductivity to be increased substantially, since this determines the electronic carrier concentration. The results with Fe^{2+} and Fe^{3+} doping are consistent with the experiments using other dopants M'' that show that when conductivity increased, the dopant in question was found to be in solid solution (either through STEM measurements of dopant distribution in the crystallites or by the appearance/absence of impurity phases by STEM or XRD).

Further, it is believed that the solubility of dopants M'' is a function of ion size. With the exception of Mn^{2+} , all of the dopants that can be effective as M' dopants have an ionic radius, in octahedral coordination, that was less than that of Fe^{2+} . This is supported by the following ionic radii values, taken from the tabulation by Shannon (1976):

$R(\text{Fe}^{2+}) = 0.78 \text{ \AA}$	$R(\text{Li}^+) = 0.76 \text{ \AA}$		
$R(\text{Fe}^{3+}) = 0.65 \text{ \AA}$	$R(\text{Mg}^{2+}) = 0.72 \text{ \AA}$	$R(\text{Mn}^{2+}) = 0.83 \text{ \AA}$	$R(\text{Ti}^{4+}) = 0.61 \text{ \AA}$
$R(\text{Zr}^{4+}) = 0.72 \text{ \AA}$	$R(\text{Nb}^{5+}) = 0.64 \text{ \AA}$	$R(\text{Ta}^{5+}) = 0.64 \text{ \AA}$	$R(\text{W}^{6+}) = 0.60 \text{ \AA}$
$R(\text{Al}^{3+}) = 0.54 \text{ \AA}$			

The temperature dependence of conductivity in the materials of the invention was measured using 2-point and 4-point electrical conductivity measurements of fired pellets pressed from powder samples prepared according to Examples 1 and 2. Both undoped and doped compositions were measured. In addition, ac (impedance spectroscopy) measurements were made on pellets prepared from undoped powder. The temperature dependence of electrical conductivity is shown in FIGS. 8 and 9 as a plot of \log_{10} conductivity against $1000/T(\text{K})$. It is seen that the doped compositions can have more than 10^7 greater conductivity than an undoped sample. While both types exhibited

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increasing conductivity with increasing temperature, indicating semiconducting behavior, the doped materials had much shallower temperature dependence. An activation energy in the range of 25 - 75 meV was determined for the highly conductive doped samples, which is reasonable for ionization of shallow acceptors or donors, while
5 an activation energy of about 500 meV was observed for the undoped sample. The high conductivity of the doped samples is maintained, with little temperature dependence, over the -20C to +150C temperature range of interest for many battery applications. Near room temperature, for example between 21C to 27C, the variation of electronic conductivity with temperature is minor, such that where a temperature within this range
10 is referred to herein, it is understood that a range of temperatures around any particular value is included.

The highly conductive samples were also subjected to a Seebeck coefficient measurement. Platinum leads were attached to two ends of a sintered sample, whereupon one end was heated to a higher temperature than the other end, and the
15 induced voltage was measured. The heated end was found to be at a negative potential relative to the cold end, exhibiting easily measured and significant potential values of -0.1 mV to -0.3 mV. This shows that the conductive LiFePO_4 compositions were p-type conductors. An undoped LiFePO_4 composition subjected to the same measurement was found to be n-type.

20 In some cases, the electrical conductivity of the samples was measured using a four-point microcontact method in order to determine the conductivity of individual crystalline grains. For these measurements, densely sintered pellets with an average grain size of about 10 micrometers were cut and polished. A co-linear array of microcontacts were used. Current probes were placed about 100 micrometers apart on
25 the polished surface, while voltage probes were placed about 10 micrometers apart. FIG. 10 shows three samples whose conductivities at the microscopic scale were measured, two being 1% Nb-doped conductive compositions sintered at 850C and 900C respectively, and one being an undoped composition sintered at 900C. Combustion IR detection showed that all three samples had low carbon content, less than 0.5 wt%. The
30 gray phase in FIG. 10 is the olivine phase, the black contrast features are porosity, and the bright contrast particles are iron phosphide phase. FIG. 11 shows the microcontact measurement geometry, in which it is seen that the inner voltage contacts are about 10 micrometers apart, or about the same separation as individual grains in the samples of

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FIG. 10. Thus the voltage contacts typically span one grain or one grain boundary. The microcontact array was placed in 12 to 15 separate locations on each sample, and the current-voltage relationship was measured at each point over a range of currents in a room-temperature laboratory. FIG. 12 shows histograms of the conductivity obtained from the measurements, in which each bar represents one location of the microcontact array. It is seen that firstly, within each sample the conductivity has a similar value from place to place showing relatively uniform conductivity across a sample. Secondly, the conductivity of the doped samples is of about the same magnitude as measured by two-point and four-point measurements across entire sintered pellets, and is several orders of magnitude greater than the conductivity of the undoped sample.

TEM observations were made of the powders of Example 2. FIG. 13 shows copies of TEM images of powders doped with 1% Nb or 1% Zr. It is seen that the average size of individual crystallites is less than about 100 nm in the Nb-doped sample, less than about 50 nm in the Zr-doped sample, and that the powder has an aggregated morphology. Energy-dispersive X-ray analysis was conducted to determine the location of residual carbon, typically present at a level determined by combustion IR analysis to be between 0.2 and 2.5 wt% depending on the firing conditions. FIG. 14 shows TEM images and corresponding chemical analyses of regions in a 1% Nb doped sample fired at 600°C and that was analysed to have about 2.4% residual carbon. This sample of relatively high residual carbon content compared to others of Example 2 was selected for TEM in order to determine if a carbon coating on the particles as practiced in prior art was present. FIG. 14 shows a particle of unreacted precursor, present in small amounts in the sample, in which carbon is found at an enriched level. In the other regions, containing the olivine phase, no carbon is detected. FIG. 15 and 16 show high resolution TEM images of olivine phase particles, in which lattice fringes are imaged. No continuous surface phase of carbon or other separate conductive compound was found. Thus it is seen that the fine particle size and increased conductivity of these samples is observed in samples without a significant amount of free carbon.

Surface area measurements are another well-known measure of effective particle size. The specific surface area was measured, using the BET method, of doped and undoped samples heat treated under several conditions. Table 4 shows results for several powder samples. It is observed that the undoped powders have a specific surface area that is typically less than about 10 m²/g for heat treatment temperatures of 600°C or

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greater. These are heat treatment conditions sufficient to provide a nearly completely crystallized powder. However, the doped compositions have much higher surface area, typically greater than 40 m²/g for 1% Zr-doped powder fired at 600C, and greater than 30 m²/g for 1% Nb-doped powder fired at 600C. In the doped samples the powder is

5 also nearly completely crystallized after firing at these temperatures although a small quantity of incompletely crystallized precursor to the olivine phase remains. Other powders doped with 0.2-1 mole % of dopants such as Al, Mg, and Ti also had specific surface areas of 35 to 42 m²/g after firing at 600C. At higher firing temperatures of 700 to 800°C the specific surface area of the doped samples remains higher than of the

10 undoped samples. Having a crystal density of 3.6 g/cm³, the diameter of monosized spheres of the compound having an equivalent specific surface area (i.e., the equivalent spherical particle size) of 40 m²/g is 21 nm, of 30 m²/g is 28 nm, of 29 m²/g is 42 nm, of 15 m²/g is 56 nm, of 10 m²/g is 83 nm, of 5 m²/g is 167 nm, and of 1 m²/g is 833 nm. Thus it is seen that the doping methods of the present example provide for complete or

15 nearly complete crystallization of the olivine structure compound while also providing for a high specific surface area, higher than that of the undoped compound under identical processing and firing conditions.

Table 4. Compositions, Firing Conditions, and Specific Surface Areas of Insulating and

20 Conductive Samples

Composition	Temp. (°C)	Container	BET area (m ² /g)	Conductivity	Color
LiFePO ₄	600	Plastic bottle	9.5	insulating	Gray
	700	Porcelain jar	3.9	insulating	Gray
	800	Porcelain jar	~1	insulating	Light Gray

LiFe _{0.99} Zr _{0.01} PO ₄	600	Porcelain jar	43.2	conductive	Black
	600	Porcelain jar	41.8	conductive	Black
	700	Porcelain jar	26.4	conductive	Black
	750	Porcelain jar	11.6	conductive	Dark gray

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$\text{LiFe}_{0.99}\text{Nb}_{0.01}\text{PO}_4$	600	Porcelain jar	34.7	conductive	Black
	800 P	Porcelain jar	15.3	conductive	Black

Without being bound by any particular interpretation, these results show that conductivities, higher than those obtained using the method and compositions of Example 1, can be obtained in a composition that is deficient in the alkali ion and excess in the other metals that would normally occupy octahedral sites in a LiFePO_4 structure. As mentioned, the results show that the solubility of the metal, M'' , was higher when the composition was formulated in this manner. Without being bound by any interpretation, it is reasonable to expect that having a deficiency of Li and excess of Mg allows one or the other octahedral site cations, Mg or Fe, to occupy octahedral sites in the structure that would normally be occupied by Li.

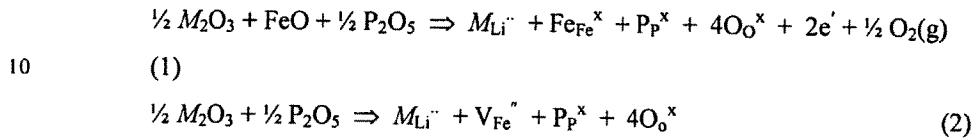
Based on the results obtained in this instance, where there is an excess of the non-alkaline metal and a deficiency of the alkali, it is believed that almost any metal added to the structure of the parent compound such that substitution of the metal onto the M1 crystallographic sites normally occupied by the main alkaline metal occurs, would have the desired effect of improving the electronic conductivity of the resulting compound.

Without being bound by any particular interpretation, we note that LiFePO_4 is found by first-principles calculations of the spin-polarized type to have an unusual band structure of the type known as a half-metal. The band gap is spin-sensitive and may in one spin have a gap of about 1 eV while in the other being a metal. It is also found that the electron effective mass is much larger than the hole effective mass, which is consistent with observation of higher electronic conductivity in a p-type conductor.

Without being bound by any particular interpretation, it is noted that a mechanism of defect formation can be understood from the observations that the increased electronic conductivity of the present materials is thermally activated and p-type, that there is not a strict proportionality between dopant concentration and conductivity, that similar increases in conductivity are possible for dopants of 2+ through 6+ valence, that a two-phase reaction exists upon delithiation, as shown in later Examples and as is seen in undoped LiFeO_4 , and that a high capacity and high rate capability are maintained over a wide range of lithiation of the doped compounds. The olivine structure has continuous networks of metal-filled anion polyhedra, including

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having the cations that occupy the M2 sites (Fe site in LiFePO₄) forming a corner-sharing network of octahedra in the (010) plane, while the cations on M1 (Li) sites form edge-sharing chains of octahedra in the [100] direction. It is noted that the substitution of a cation M that is supervalent to Li⁺ in the composition Li_{1-x}M_xFePO₄ is normally expected to result in donor doping. In oxides, aliovalent solutes can be compensated by electronic or ionic defects. The following point defect reactions (in Kröger-Vink notation), illustrate these mechanisms for an M^{3+} cation that is respectively compensated by electrons or by cation vacancies on the M2 site:



In the first instance, electroneutrality is given by $[M_{Li}^{\bullet\bullet}] = n$, namely the dopant acts directly as a donor species. If the second mechanism is dominant, electroneutrality is given by $[M_{Li}^{\bullet\bullet}] = 2[V_{Fe}^{\bullet\bullet}]$, in which case the donor and vacancy charge-compensate one another and no direct effect on the electronic carrier concentration is expected. However, it can be shown that in this instance as well, secondary defect equilibria should lead to an increase in the n -type conductivity. Neither of these simple mechanisms can explain a material of high p -type conductivity. An excess of acceptor point defects above and beyond the dopant concentration, or a large difference between hole and electron mobilities as discussed earlier, are necessary. Possible acceptors in the LiFePO₄ structure are cation vacancies (V_{Li}^{\bullet} , V_{Fe}^{\bullet}), or oxygen interstitials (O_i^{\bullet}). The latter defect is unlikely given the nearly hexagonal close-packed oxygen sublattice in olivine, which should result in a high anion vacancy formation energy.

A mechanism whereby cation doping on the M1 sites allows the stabilization of solid solutions with a net cation deficiency, that is, where the doped olivine endmember has a solid solution of composition Li_{1-a-x}M_xFePO₄ or Li_{1-x}M_xFe_{1-b}PO₄, in which a and b are M1 or M2 vacancy concentrations respectively, is consistent with the results. If the net charge due to a and b exceed that due to x , then the material will have a net excess of acceptor defects (Fe³⁺ ions). Taking for example an M^{3+} dopant, the respective valences for a lithium deficient solid solution are Li¹⁺_{1-a-x}M³⁺_x(Fe²⁺_{1-a+2x}Fe³⁺_{a-2x})(PO₄)³⁻. It is noted that lithium deficiency is particularly likely under high temperature firing conditions due to lithium volatility. The above defect mechanism is analogous to allowing an extension

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of the solid solution field for the pure Li-rich endmember phase to cation deficient solid solutions, $\text{Li}_{1-x}\text{FePO}_4$. We recall that pure LiFePO_4 has been observed to decompose immediately to two co-existing phases upon delithiation, LiFePO_4 and FePO_4 , thereby pinning the Li chemical potential and resulting in the flat intercalation voltage vs. lithium concentration. Thus the insulating behavior of undoped LiFePO_4 throughout electrochemical cycling suggests negligible mixed ($\text{Fe}^{2+}/\text{Fe}^{3+}$) iron valency in either phase. The retention of either lithium or iron deficiency in the highly lithiated solid solution can therefore result in charge compensation by Fe^{3+} and p -type conductivity.

Regarding the delithiated FePO_4 endmember phase, our electrochemical data in later Examples indicate that it also retains high electronic conductivity throughout cycling. The influence of M1 site cation doping is expected to be quite different for this phase. Starting with pure FePO_4 , in which all iron is trivalent, cation doping will result in the formation of divalent iron: $M^{2+}_x(\text{Fe}^{2+}_{3x}\text{Fe}^{3+}_{1-3x})\text{PO}_4$. This composition is obtained upon delithiation of the solid solution given earlier. The dopant in this instance may be viewed as an "interstitial" cation donor, occupying normally unoccupied M1 sites, and n -type conductivity should result. During operation as a lithium storage material, the present materials may be a two-phase material, one phase p -type and the other n -type, that change in their relative proportions as the overall lithium concentration changes. A transition from p - to n -type conductivity may be measurable for the two-phase material as a whole as delithiation proceeds. This behavior may be observed whether the cation dopant M occupies the M1 site, or preferentially occupies the M2 site and displaces Fe to the M1 site.

The room temperature conductivity of some of the compounds of the invention exceeds that of the well-established intercalation cathodes LiCoO_2 and LiMn_2O_4 in their lithiated (discharged) states. At these high levels of electronic conductivity, lithium ion transport is likely to limit the overall rate of intercalation and deintercalation. That is, the effective lithium chemical diffusion coefficient is likely to be limited by lithium transport (i.e., the ionic transference number t_{Li} is ~ 0). Because it is known that delithiation of LiFePO_4 results in coexistence of two phases, lithium ingress and egress from particles of the storage material requires growth in the amount of one phase and a decrease in the amount of the other. Without being bound by any particular interpretation of the rate-limiting microscopic mechanism of phase transformation, it is

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understood that a decrease in the crystallite size is beneficial to ion transport. At the same time, it is necessary to simultaneously accommodate electron flow to and from the particles. The structure of the materials of the invention are almost ideal for providing optimal mixed electronic-ionic transport in a battery system, having a porous aggregate structure in which the nanoscale primary crystallites can be surrounded by the electrolyte, allowing lithium ion transport through a very small cross-sectional dimension, while remaining electronically "wired" together through the sinter necks. For materials in which electronic transport is limiting, it can still be beneficial to decrease the crystallite size, as the potential drop across particle is less for a material of higher conductivity. (If ion transport is limiting, further increases in the electronic conductivity are not expected to improve the rate capability of a single particle significantly, but can improve the electronic conductivity of a network of particles such as that present in a typical composite electrode.)

Having a fine primary crystallite size due to doping as provided by the present invention provides high rate capability. Therefore, another feature of the materials of the present invention is a structure characterized by primary crystallites having at least a smallest dimension that is less than 200 nm, preferably less than 100nm, still preferably less than 50 nm, and still more preferably less than 30nm. According to the invention the individual crystallites of the stated sizes are typically joined by sintering, forming an interconnected but porous network. In some cases, an average of at least 50% of the surface area of the primary crystallites is exposed so that it can contact the electrolyte. To determine the percentage of exposed surface area, the following procedure can be used: the average primary particle size and shape was measured, for instance by electron microscopy, and the surface area per unit mass can be thus computed. This would be the surface area that would result for completely isolated particles. The specific surface area of the powder can then be measured and compared to the first number. The latter should be at least 50% of the former. In accordance with having a very small primary crystallite size and aggregates that are not highly densified, the specific surface areas of the materials of the invention are preferably greater than about 10 m²/g, more preferably greater than about 20 m²/g, more preferably greater than about 30 m²/g, and still more preferably greater than about 40 m²/g.

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It is understood that olivines with other metals partially or completely substituted for Fe, including but not limited to LiMnPO_4 and LiCoPO_4 , or others in the family of polyanion compounds, including but not limited to those with continuously joined networks of transition metal filled polyhedra within the structure, may enjoy the benefits of improved electronic conductivity, reduced crystallite size, high reversible charge capacity, high rate capability, and other benefits described herein when they are doped or processed according to the invention.

Example 3. Electrode Fabrication and Electrochemical Tests

A composition $\text{Li}_{0.998}\text{Nb}_{0.002}\text{FePO}_4$ was prepared as described in examples 1 and 2 using lithium carbonate, niobium phenoxide, iron oxalate, and ammonium dihydrogen phosphate, and heat treated according to the procedure labeled as HT1 shown in Table 2. The resulting powder was black and conductive, and was cast as an electrode coating on an aluminum foil current collector, using a standard formulation of 85 wt% of said composition, 10 wt% SUPER P™ carbon, and 5 wt% PVDF binder. γ -butyrolactone was used as the solvent. The positive electrode (cathode) coating was tested against a lithium metal foil counterelectrode (anode) in a standard cell assembly using CELGARD® 2400 separator film and EC:DMC (+1M LiPF_6) as the electrolyte. Galvanostatic tests were performed at several current rates. FIG. 17A shows the first electrochemical cycle at C/30 rate, in which it is seen that a capacity of about 150 mA/g is obtained. A flat voltage plateau is observed, indicating a two-phase equilibrium of constant lithium chemical potential. FIG. 17B shows capacity vs. cycle number for this electrode at a 1C rate (150 mA/g), to about 260 cycles. FIG. 17C shows that the coulombic efficiency vs. cycle number at 1C rate (150 mA/g) is generally greater than about 0.997. These results show that this material of the invention had good performance as a storage cathode for rechargeable lithium battery systems, at practical rates of charge and discharge, without requiring special procedures, such as coating with conductive additives.

Example 4. Electrode Fabrication and Electrochemical Tests of the Lithium Storage

Compounds and Electrodes of the Invention at High Discharge Rates

The electrochemical performance of the undoped and doped powders of Examples 1 and 2 were evaluated by using them in electrodes of a variety of formulations and testing said electrodes under a wide range of conditions as the positive

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electrode in a liquid electrolyte cell, using lithium metal foil as the negative electrode.

Table 5 lists several of the electrode formulations that were prepared and tested. All samples were tested using CELGARD® 2400 or 2500 separator film and 1:1 EC:DEC with 1M LiPF₆ liquid electrolyte.

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Table 5. Lithium Storage Materials and Electrode Formulations

Sample	Active Materials Composition and Heat Treatment	Specific Surface Area (m ² /g)	Electrode Formulation (wt percentages)	Active Material Loading (mg/cm ²)
A	LiFePO ₄ , 700°C/Ar	3.9	Cathode/Super-P/Kynar 461 79/10/11	5.3
B	LiFePO ₄ , 700°C/Ar	3.9	Cathode/Super-P/Kynar 461 79/10/11	7.8
C	(Li _{0.99} Zr _{0.01})FePO ₄ , 600°C/Ar	~40	Cathode/Super-P/Alfa-Aesar PVdF 78.3/10.1/11.6	>3.9
D	(Li _{0.99} Zr _{0.01})FePO ₄ , 600°C/Ar	~40	Cathode/Super-P/Alfa-Aesar PVdF 78.4/10.0/11.6	2.5
E	(Li _{0.99} Zr _{0.01})FePO ₄ , 600°C/Ar	41.8	Cathode/Super-P/Kynar 2801 79/10/11	4.0
F	(Li _{0.99} Zr _{0.01})FePO ₄ , 600°C/Ar	41.8	Cathode/Super-P/Kynar 2801 79/10/11 plasticized	4.3
G	(Li _{0.99} Zr _{0.01})FePO ₄ , 600°C/Ar	41.8	Cathode/Super-P/Kynar 2801 79/10/11 plasticized	4.4
H	(Li _{0.99} Zr _{0.01})FePO ₄ , 700°C/Ar	26.4	Cathode/Super-P/Kynar 461 79/10/11	5.3
I	Li(Fe _{0.98} Ti _{0.02})PO ₄ , 600°C/Ar	~40	Cathode/Super-P/Kynar 461 79/10/11	5.9
J	(Li _{0.998} Nb _{0.002})FePO ₄ , 600°C/Ar	~40	Cathode/Super-P/Alfa-Aesar PVdF 85/10/5	-

Table 5, Sample D.

A composition ($\text{Li}_{0.99}\text{Zr}_{0.01}\text{FePO}_4$), fired at 600°C in Ar according to the methods of Example 2, and having a specific surface area of about 40 m²/g, was formulated into an electrode by mixing 78.4 wt% of the active material, 10.0 wt% of SUPER P™ carbon, and 11.6 wt% Alfa-Aesar PVdF as the binder, using γ -butyrolactone as solvent. The mixing was done in a small plastic container containing one Teflon® ball using a dental amalgamator (Wig-L-Bug) for 5 minutes. Mixed suspensions were cast onto aluminum foil current collectors, dried, and pressed at 4 tons/cm². Electrochemical test samples were cut from the pressed castings and assembled in stainless steel test cells with lithium metal foil (Alfa Aesar, Ward Hill, MA, USA) as the counterelectrode and CELGARD® 2400 (Hoechst Celanese, Charlotte, NC, USA) as the separator. The liquid electrolyte used was 1:1 by wt ethylene carbonate and diethyl carbonate with 1M LiPF₆ added as the conductive salt.

Figure 18A shows the charge and discharge capacities of a cell with about 2.5 mg/cm² loading of the active material, observed in continuous cycling at rates varying from 15 mA/g (C/10) to 3225 mA/g (21.5C) between the voltage limits of 2.8-4.2V, at room temperature. It is noted that a stable capacity is obtained upon cycling over a wide range of rates, to more than 150 cycles. Figure 18B shows corresponding charge-discharge curves for the doped sample, in which there is only a modest polarization, with a clear voltage plateaus at ~3.1V even at a discharge rate of 21.5C. Comparing with published data for LiFePO₄, it is clear that the low doping levels used to increase conductivity and increase specific surface area do not decrease the storage capacity at low rates, but greatly increase the power density that is possible. The low polarization is attributed to the high electronic conductivity at the particle scale. Thus this electrode made using a compound of the invention is seen to have high energy density at much higher current rates than previously seen for undoped LiFePO₄.

Table 5, Sample C.

An electrode prepared as described for Sample D of Table 5, and having >3.9 mg/cm² loading of active material, was assembled in a Teflon® and stainless steel Swagelok® test vessel with lithium metal foil (Alfa Aesar, Ward Hill, MA, USA) as the counterelectrode and CELGARD® 2400 (Hoechst Celanese, Charlotte, NC, USA) as

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separator. The liquid electrolyte used was 1:1 by wt ethylene carbonate and diethyl carbonate with 1M LiPF₆ added as the conductive salt.

Figure 19A shows discharge capacities measured at 42°C observed in continuous cycling tests. For the curve labeled 0.2C, the cell was charged and discharged at a current rate of 0.2C (30 mA/g) between the voltage limits of 2-4.2V. For the other curves, the cell was charged at a rate of 1.1C (165 mA/g) and then discharged at the rates shown. It is seen that this cell maintains a significant discharge capacity and relatively little polarization upon discharging at rates as high as 66.2C (9.93 A/g). Compared to previously reported electrochemical test data for LiFePO₄, this cell can be discharged at a remarkably high power density while still having significant energy density.

Table 5, Sample F, E, G, H.

Sample F was prepared from a composition (Li_{0.99}Zr_{0.01})FePO₄, fired at 600°C in Ar according to the methods of Example 2, and having a specific surface area of 41.8 m²/g. It was formulated into an electrode by mixing 79 wt% of the active material, 10 wt% of SUPER P™ carbon, and 11 wt% Kynar 2801 binder in γ-butyrolactone as solvent, using the procedures of Sample D and C. After casting and drying, the coating was immersed in a plasticizing solvent of 15 wt% propylene carbonate in methanol, then pressed and dried. The resulting positive electrode (cathode) was tested against a lithium metal foil counterelectrode (anode) in a Swagelok cell assembly using CELGARD® 2500 separator film and 1:1 EC:DEC with 1M LiPF₆ liquid electrolyte.

FIG. 20 shows discharge curves for this cell measured by the constant-current constant-voltage (CCCV) method whereby the cell was first charged at 0.5C rate (75 mA/g), then held at the upper limiting voltage of 3.8V until the charging current decayed to 0.001 mA, before discharging to 2V at the stated rate. Note that in comparison to FIG. 19, the initial linear behavior upon discharge is not seen, indicating that the linear region is a capacitive response due to incomplete equilibration in the cell. (In later calculations of the energy density of cell tested in continuous cycling, the capacity of this linear region is not included.) The results in FIG. 20 show quite remarkably that even at a 50C (7.5 A/g) discharge rate, about half of the capacity available at C/5 rate is provided by the cell.

FIG. 21 compares the discharge energy density of Sample F with Samples E, G, and H from Table 5. All tests were conducted at 22-23°C. Sample G was prepared in

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the same manner as Sample F, and was tested by continuous cycling according to the procedure of Sample C. Sample E was prepared and tested in the same manner as Sample G, except that the electrode was not plasticized. Sample H was prepared from a powder fired to a higher temperature than the others in FIG. 21, 700C in Ar, and has a lower specific surface area of 26.4 m²/g, and used Kynar 461 binder, but was otherwise processed and tested in like manner. It is seen that all four of the samples in FIG. 21 exhibit a remarkably high capacity at high discharge C rates.

Table 5, Samples A and B

Samples A and B were prepared from undoped LiFePO₄, which after firing at 700C has a relatively low specific surface area of 3.9 m²/g. The electrodes were prepared and tested in like manner to Sample H in Table 5, and the results are shown in FIG. 22, measured at 23, 31, and 42°C. Unlike the results in FIG. 21, however, the undoped samples show greatly inferior discharge capacity that falls to about 20 mAh/g by about 5C (750 mA/g) rate. It is also seen in FIG. 22 that heating to a temperature of 42°C does not significantly improve the discharge capacity.

Comparison with Literature Data

Electrochemical test results have been reported for several LiFePO₄-based electrodes in the published literature. FIG. 23 compares the results from Sample F in Table 5 to results from several published papers. It is seen that the electrodes of the invention have markedly higher discharge capacity at high rates, whereas the literature data typically shows a rapid decrease in capacity with increasing rate at rates below 5C or 10C rate. This comparison illustrates the novel high performance properties of the lithium storage materials and electrodes of the current invention.

Energy Density vs. Current Density

In FIGS. 24 – 27, we show the discharge energy density available from the total mass of storage compound available in several electrodes of Table 5, plotted against the current per gram of storage material. The energy densities are obtained by integrating the voltage vs. charge capacity curves. In FIG. 24, results from Sample F are shown for a measurement temperature of 22°C; in FIG. 25, results for Sample G are shown for

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measurement temperatures of 23, 31, and 42°C; in FIG. 26, results for Sample I measured at 23°C; and in FIG. 27, results are shown for Sample A for measurement temperatures of 23, 31, and 42°C. Comparing FIGS. 24-26 with FIG. 27, the vast improvement in the energy density of the lithium storage materials of the invention compared to undoped LiFePO_4 is clearly seen

Example 5: Storage Battery Cells

Example 4 illustrates the high discharge capacity available from the lithium storage compounds of the invention, and electrodes utilizing said compounds, at high discharge rates. Having shown clearly the improved electrochemical properties of the lithium storage compounds and electrodes of the invention, we now illustrate storage battery cells of exceptional power density and high energy density based on these compounds and electrodes.

It is well-known that typical lithium-ion batteries based on laminated electrodes and designed for high energy density contain 25-35% by weight and 13-18% by volume of the positive electrode storage compound, typically LiCoO_2 . While more detailed calculations of the weight and volume fractions of materials are used for specific designs, these approximate values provide an adequate basis for determining the energy density and power density of conventional cell designs utilizing the present lithium storage compounds. Accounting for the 29% lower crystal density of LiFePO_4 compared to LiCoO_2 , and assuming a somewhat lower packing density due to the high specific surface area, it is conservatively estimated that an optimized cell could contain 10-20 wt% of the positive electrode active material. Using the results of Example 4 for electrodes tested against lithium metal negative electrodes, and taking into account its slightly lower cell voltage when used in conjunction with a carbon electrode (3.25 vs. 3.7 V), the power density – energy density results shown in FIG. 28 are obtained. Results are shown for 10 wt%, 15 wt%, and 20 wt% of the positive electrode active material. Power and energy densities for complete discharge of a cell of 800-1500 W/kg and 30-60 Wh/kg at a 20C (3 A/g) rate, 1500-4200 W/kg and 15-30 Wh/kg at a 50C (7.5 A/g) rate, and 2500-5000 W/kg and 5-10 Wh/kg at a 80C (12 A/g) rate, are obtained. Such cells could provide power densities not possible in current nickel metal-hydride (400-1200 W/kg, 40-80 Wh/kg) and lithium-ion battery technology (800-2000 W/kg, 80-170

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Wh/kg). These capabilities, in a low-cost and ultra-safe storage material, may be especially attractive for high power and large battery applications including but not limited to power tools and hybrid and electric vehicles.

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Example 6. Doping From Milling Media and Containers

This example shows that doping to yield high electronic conductivity can be accomplished by using suitable milling media and containers. It also shows that the high electronic conductivity of the materials of the invention is obtained without excessive carbon or other conductive additives. Table 6 shows the results of carbon and zirconium analysis of several materials prepared according to the methods of Examples 1 and 2. It is seen that milling with 3/8" ZrO₂ milling media can add a detectable concentration of Zr to the samples. Amongst the nominally undoped samples, a high conductivity of about 10⁻³ S/cm is observed when the Zr concentration from the milling media is 0.018.

15 Taking this added Zr into account, the composition of the sample is of type Li_{1-a}Zr_aFePO₄, similar to other high conductivity samples. It is also seen that the polypropylene milling jar has added some excess carbon to this sample. When 1/4" ZrO₂ milling media are used, negligible Zr doping occurs. An undoped sample fired at 800C has 0.25 wt % carbon, and a low conductivity of 10⁻⁸ S/cm.

20 Lightly doped samples such as in Table 1 that have been milled with zirconia milling media can thus also be doped with Zr in addition, improving the conductivity.

The four Zr and Nb doped samples, were formulated to have Li_{1-a}M_aFePO₄ composition and have high electronic conductivity. The concentration of carbon is less than 2 weight percent in one instance, and less than 1 weight percent in the other three instances. The sample of highest conductivity, 10⁻² S/cm, has the lowest carbon concentration, only 0.32 weight percent, nearly the same as the highly insulating undoped samples. The sample with the highest carbon concentration has the lowest conductivity. These results show that the high electronic conductivity of doped samples is not correlated with carbon concentration but instead with doping as described herein.

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Table 6. Carbon analysis of conductive lithium iron phosphate materials.

Composition	Preparation Method	Carbon (wt%)	Zr (wt%)	Conductivity 2-probe (S/cm)
Undoped (large batch)	Polypropylene bottle,	0.25	0.009	10 ⁻¹⁰

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700° C	3/8" ZrO ₂ media			
Undoped (Li _{0.99} FePO ₄) 700° C	Polypropylene bottle, 3/8" ZrO ₂ media	2.41	0.018	(~10 ⁻³)
Undoped 800° C	Porcelain jar, 1/4" ZrO ₂ media	0.25		10 ⁻⁸
1% Zr doped 700° C	Porcelain jar, 1/4" ZrO ₂ balls	1.46		10 ⁻⁴
1% Zr doped 800° C	Porcelain jar, 1/4" ZrO ₂ balls	0.86		10 ⁻³
1% Nb doped 800° C	Porcelain jar, Tiny ZrO ₂ balls	0.56		10 ⁻³
1% Nb doped 800° C	Polypropylene bottle, 3/8" ZrO ₂ media	0.32		10 ⁻²

Example 7. Compositions With Dopant Not in Solid Solution

In this example, as in Example 1, it is shown that when a doped composition similar to the preceding examples of high electronic conductivity is prepared, but the dopant is not in solid solution, then the composition is not conductive. In Example 2, it was shown that a composition (Li_{0.99}Nb_{0.01})FePO₄ has markedly improved conductivity and electrochemical storage properties compared to an undoped LiFePO₄ when the Nb dopant is in solid solution in the crystal lattice. Here it is shown that the same composition prepared with the dopant not in solid solution, but precipitated as a secondary phase, is substantially insulating.

1 mole % Nb-doped LiFePO₄ was prepared using iron acetate, Fe(CH₃COO)₂ as the Fe precursor. Niobium phenoxide, Nb(C₆H₅O)₅ was used as the source of the dopant. The theoretical content of Fe in iron acetate is 32.12 wt%. However, the iron content of iron acetate frequently deviates from the ideal value. Thus it was expected that the composition of the compound would deviate from a nominal composition (Li_{0.99}Nb_{0.01})FePO₄ that provides good electronic conductivity. A batch of powder was formulated according to the following proportions of starting materials:

<u>1 mole % Nb-doped LiFePO₄</u>	
	~4 g batch
NH ₄ H ₂ PO ₄	2.3006 g (99.998%, Alfa-Aesar)
Li ₂ CO ₃	0.7316 g (99.999%, Alfa-Aesar)
Fe(CH ₃ COO) ₂	3.7867 g (99.9%, Alfa-Aesar)
Nb(C ₆ H ₅ O) ₅	0.1116 g (Alfa-Aesar)

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Each of the components was weighed in an argon-filled glove box. They were then removed from the glove box and ball milled, using zirconia milling balls (~1/4" diameter, 400-450g total weight) in a porcelain milling jar (300ml capacity) for 24 hours in acetone (150-160ml) at 230 rpm. The milled mixture was dried at a temperature not exceeding 80°C, and then ground with a mortar and pestle in the argon-filled glove box. The mixture was then heat treated in two steps. A first heat treatment at 350°C for 10 hours was conducted in a flowing Ar (99.999% purity) atmosphere (>400cc/min). The powder sample was then ground in laboratory air atmosphere, using a mortar and pestle, and subjected to a second heat treatment at a higher temperature (600°C to 700°C) for 20 hours, in flowing Ar gas (>400cc/min). The heating and cooling rates for each step were 5°C/min. Before heating, purging of the furnace tube in flowing Ar for about 1 hour was conducted.

In contrast to the cases where iron oxalate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) is used as the starting materials, a 2-probe resistance measurement of this sample showed that the conductivity is less than 10^{-7} S/cm at a temperature of 23-27°C. X-ray diffraction of a sample fired at 600°C for 20h in Ar showed that it was predominantly LiFePO_4 but had a small amount of an unidentified secondary phase. TEM analysis showed that the dopant Nb was not detectable inside the particles, but was segregated as a secondary phase. Furthermore, the specific surface area of this material was much lower than it is in samples prepared so that the Nb dopant is in solid solution, being $14.3 \text{ m}^2/\text{g}$ for 600°C firing. Thus it is shown that in this material, when a substantial amount of the added Nb dopant is not in solid solution in the crystalline particles, an increased conductivity is not observed, nor is the advantageous feature of metal additives of diminishing the crystallite size realized. It is understood that the iron acetate precursor, being a suitable reactant for the formation of LiFePO_4 , is suitable for producing highly conductive compositions when the overall composition is known and more precisely controlled.

Example 8. Solid State Reaction Synthesis of LiFePO_4

This example describes the preparation of LiFePO_4 , using wustite iron oxide, FeO, and lithium metaphosphate, LiPO_3 , as precursors. An advantage of these precursors is that they form a closed or nearly closed reaction system, by which it is meant that upon heat treatment, few if any gaseous species are produced as a reaction by product. Adjustments to the relative amounts of the reactants, and the addition of other

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constituents such as the dopants in the form of oxides can be used in order to obtain compositions comprising the materials of the invention.

A batch of 6 g LiFePO_4 was prepared by using starting materials of the following amounts: 2.733 g FeO (99.5%, Alfa-Aesar, Ward Hill, MA, USA) and 3.267 g LiPO_3 (97%, City Chemical LLC., West Haven, CT, USA). The components were weighed in an Ar-filled glove box, and transferred to a porcelain jar and ball-milled in acetone for 48 h using zirconia milling balls. The acetone was evaporated from the milled powder at a low temperature ($<100^\circ\text{C}$), and the dried powder was ground with a mortar and pestle and pressed into pellets. The pellets were embedded in loose powder of the same material and placed in alumina crucibles and subjected to a single heat treatment under Ar atmosphere at $550\text{--}900^\circ\text{C}$ for 20 h.

The heat-treated samples were light to medium grey in color. Predominantly single-phase LiFePO_4 was obtained for all heat-treatment temperatures, as identified by X-ray diffraction. Minor amounts of Fe_2P and Fe phases were detected by XRD at heat-treatment temperatures at and above 600°C .

Example 9. Solid State Reaction Synthesis of Nb-doped LiFePO_4

Conductive compositions of the invention are obtained using the starting materials and basic procedure of Example 8, and by adding dopants in the form of oxides, hydroxides or alkoxides to obtain the dopant metal ion in the preferred valence state. A conductive sample with the nominal formulation $\text{LiFePO}_4 + 1 \text{ mole\% Nb}$ was prepared using the precursors of Example 8 and adding a small amount of the dopant niobium phenoxide, $\text{Nb}(\text{C}_6\text{H}_5\text{O})_5$. A batch of about 1g powder was prepared by using 0.4530 g FeO , 0.5416 g LiPO_3 and 0.0352 g $\text{Nb}(\text{C}_6\text{H}_5\text{O})_5$ (99.99%, Alfa-Aesar, Ward Hill, MA, USA). The powders were milled, as described in Example 6, and then pressed into pellets and heat-treated under Ar atmosphere at 600°C for 20 h. Some sintered pellets were also annealed at 850°C to obtain more densified samples or samples with more coarsened crystallites.

In contrast to the undoped powder of Example 8, the resulting powder was dark grey in color, which gave an indication of increased electronic conductivity, compared to the undoped sample. X-ray diffraction analysis showed predominantly a single crystalline phase of the triphylite LiFePO_4 structure. Resistance measurements were

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made using a two-contact method with metal probes located about 5 mm apart on the fired pellets, and showed a resistivity of about 150 k Ω , in contrast to the insulating sample of Example 8, which when made by the same procedure and from the same starting materials except for the absence of doping with niobium phenoxide showed a resistance of >200 mega ohms (M Ω). Thus it is shown that the doped compositions of the invention prepared according to the methods of this example provide an increased electronic conductivity compared to an undoped composition.

Example 10. Solid State Reaction Synthesis of Conductive LiFePO₄

In this example, doped LiFePO₄ with increased electronic conductivity is prepared using the starting materials and methods of Example 8 and 9, except that the conductive compositions of the invention are obtained by adding dopants in the form of oxides wherein the dopant are in the preferred final valence state, including but not limited to TiO₂, Nb₂O₅, Ta₂O₅, ZrO₂, Al₂O₃, MgO, or WO₆. The dopant oxide is added to the starting mixture of reactants in a quantity sufficient to give a desired concentration in the final product. Using the mixing and firing procedures of Examples 8 and 9, conductive compositions of the invention are obtained.

Example 11. Solid-state Reaction Synthesis

This example describes the all-solid state reaction synthesis of LiFePO₄ or conductive doped LiFePO₄, using wustite iron oxide, FeO, lithium oxide, Li₂O, and phosphorous(V) oxide, P₂O₅, as precursors to the major metallic constituents and metal alkoxides and metal oxides as the source of the dopants. This set of precursors also forms a closed or nearly closed reaction system, from which few if any gaseous species are evolved during synthesis.

A batch of 12 g LiFePO₄ was prepared by using starting materials of the following amounts: 5.463 g FeO (99.5%, Alfa-Aesar, Ward Hill, MA, USA), 1.136 g Li₂O (99.5%, Alfa-Aesar, Ward Hill, MA, USA) and 5.398 g P₂O₅ (99.99%, Alfa-Aesar, Ward Hill, MA, USA). The components were weighed in an Ar-filled glove box, transferred to a polypropylene jar and ball-milled for 48 h using zirconia milling balls. Special precautions were taken to avoid any exposure of the reactant mixture to air, due to the very hygroscopic nature of P₂O₅. For instance, a liquid milling medium (e.g. acetone) was not added prior to milling. The dry, milled powder was extracted from the milling

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jar in the glove box, ground with mortar and pestle and pressed into pellets. The pellets were placed in alumina crucibles and subjected to a single heat treatment at 550°C or 850°C for 20 h., after which the samples were found by X-ray diffraction to contain LiFePO₄ as the major crystalline phase. Doped samples are prepared in the same
5 manner, except with the addition of a dopant salt such as a metal alkoxide or metal oxide prior to the mixing and milling steps.

Example 12. Solid-state Reaction Synthesis

This example describes the preparation of undoped or doped LiFePO₄, using iron
10 oxalate, FeC₂O₄·2H₂O, and lithium metaphosphate, LiPO₃, as precursors. Gaseous species formed during synthesis are limited to one formula unit carbon dioxide CO₂, one formula unit carbon monoxide CO and two formula units water H₂O per formula unit reacted FeC₂O₄·2H₂O.

A batch of 1 g LiFePO₄ was prepared by using starting materials of the following
15 amounts: 1.134 g FeC₂O₄·2H₂O (99.99%, Aldrich, Milwaukee, WI, USA) and 0.5410 g LiPO₃ (97%, City Chemical LLC., West Haven, CT, USA). The components were weighed in an Ar-filled glove box, and ball milled in acetone in a porcelain jar for about 24 h, using zirconia milling balls. The acetone was evaporated from the milled powder at a low temperature (<100°C), and the dried powder was ground using a mortar and pestle.
20 The milled powder was heat treated at 350°C for 10 h under flowing Ar gas. The heat-treated powder samples were then ground again with a mortar and pestle and pressed into pellets before a second heat-treatment step. The pellets were placed in alumina crucibles and heated to 600°C or 700°C for 20 h under Ar gas. X-ray diffraction showed that a predominantly single-phase LiFePO₄ was obtained for both heat-treatment temperatures.
25 A minor amount of another detectable phase (2θ ~ 27, 28, 30 and 31°) was also observed. Doped samples are prepared in the same manner, except with the addition of a dopant salt prior to mixing and milling.

Example 13. Solid-state Reaction Synthesis

30 This example describes the preparation of undoped or doped LiFePO₄, using iron oxalate, FeC₂O₄·2H₂O, lithium oxide, Li₂O, and phosphorous(V) oxide, P₂O₅, as precursors. The formation of gaseous species during synthesis is limited to one formula

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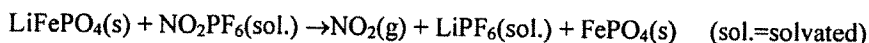
unit carbon dioxide CO₂, one formula unit carbon monoxide CO and two formula units water H₂O per formula unit reacted FeC₂O₄·2H₂O.

A batch of 1 g LiFePO₄ was prepared by using starting materials of the following amounts: 1.134 g FeC₂O₄·2H₂O (99.99%, Aldrich, Milwaukee, WI, USA), 0.09421 g
 5 Li₂O (99.5%, Alfa-Aesar, Ward Hill, MA, USA) and 0.4475 g P₂O₅ (99.99%, Alfa-Aesar, Ward Hill, MA, USA). The components were weighed in an Ar-filled glove box, and dry-milled in a porcelain jar for about 24 h using zirconia milling balls. The milled powder was extracted from the milling jar in the glove box and ground using a mortar and pestle. The powder was then heat treated at 300°C for 10 h under flowing Ar gas,
 10 ground again and pressed into pellets before a second heat treatment step. The pellets were placed in alumina crucibles and heated to 600°C or 700°C for 20 h under Ar gas. X-ray diffraction showed a predominantly single-phase LiFePO₄ for both heat-treatment temperatures. A minor amount of another detectable phase (2θ ~ 27 and 28°) and possibly a minor amount of Fe₃O₄ was also observed. Doped samples are prepared in the same
 15 manner, except with the addition of a dopant salt prior to mixing and milling.

Example 14. Chemically Delithiated Doped Conductive LiFePO₄

This example describes the chemical delithiation of a doped and conductive LiFePO₄, after which it remains highly electronically conductive as predominantly an
 20 FePO₄ phase. The chemical reduction of LiFePO₄ was conducted by the addition of a strong reducing agent, in this case nitronium hexafluorophosphate, NO₂PF₆, to a suspension of the starting material and acetonitrile, CH₃CN. Nitrogen dioxide gas, NO₂, and solvated lithium hexafluorophosphate, LiPF₆, is formed during the reaction together with the reduced FePO₄, according to:

25



Specifically a powder of (Li_{0.99}Nb_{0.01}) FePO₄ was delithiated. To obtain a relatively complete level of delithiation, the molar ratio NO₂PF₆ : (Li_{0.99}Nb_{0.01}) FePO₄
 30 was set to 2:1. For a batch of 0.6 g (Li_{0.99}Nb_{0.01}) FePO₄ (prepared according to Example 2), an amount of 1.453 g of NO₂PF₆ (98%, Matrix Scientific, Columbia, SC, USA) was used. Both reactants were weighed in an Ar-filled glove box and transferred to a filtering

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flask equipped with a rubber stopper. A thin glass tube was fitted through a hole in the rubber stopper and a silicone tube was fitted to the tubulation opening on the flask side. 100 ml of acetonitrile (99.998%, anhydrous, Alfa-Aesar, Ward Hill, MA, USA) was added to the beaker, and the glass tube was adjusted so that the tip was positioned under
5 the liquid surface. The resulting concentration of NO_2PF_6 in the solution was *ca.* 0.08 M. A flow of Ar gas was introduced at the glass tube end, so that the gaseous species formed during the reaction were led away through the silicone tube to an exhaust hood. The reaction was allowed to proceed for 24 h, while stirring with a magnetic stirrer. The resulting powder was separated from the solution by filtering through a Büchner funnel
10 equipped with filter paper (#595, Schleicher & Schuell). The powder was thoroughly rinsed in pure acetonitrile and dried under vacuum for two hours. The remaining powder was analysed by X-ray diffraction and showed a single-phase orthorhombic FePO_4 structure. The powder was black in color, and when pressed into a pellet, was highly conductive. Thus this example shows that the compounds of the invention remain highly
15 electronically conductive upon delithiation, and that a partially delithiated compound comprises two phases, one relatively highly delithiated and the other relatively delithiated, both of which are electronically conductive.

Those skilled in the art would readily appreciate that all parameters and
20 configurations described herein are meant to be exemplary and that actual parameters and configurations will depend upon the specific application for which the systems and methods of the present invention are used. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. It is, therefore, to be understood
25 that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described. Accordingly, those skilled in the art would recognize that the use of an electrochemical device in the examples should not be limited as such. The present invention is directed to each individual feature, system, or method
30 described herein. In addition, any combination of two or more such features, systems or methods, if such features, systems or methods are not mutually inconsistent, is included within the scope of the present invention.

What is claimed is:

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CLAIMS

1. A compound comprising a composition $A_x(M'_{1-a}M''_a)_y(XD_4)_z$,
 $A_x(M'_{1-a}M''_a)_y(DXD_4)_z$, or $A_x(M'_{1-a}M''_a)_y(X_2D_7)_z$, having a conductivity at 27° C of at
5 least about 10^{-8} S/cm, wherein A is at least one of an alkali metal or hydrogen, M' is a
first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, boron,
aluminum, silicon, vanadium, molybdenum and tungsten, M'' is any of a Group IIA,
IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least
one of oxygen, nitrogen, carbon, or a halogen, $0.0001 < a \leq 0.1$, and x is equal to or
10 greater than 0, y and z are greater than 0 and have values such that x, plus y(1-a) times a
formal valence or valences of M', plus ya times a formal valence or valence of M'', is
equal to z times a formal valence of the XD_4 , X_2D_7 , or DXD_4 group.

2. A compound comprising a composition $(A_{1-a}M''_a)_xM'_y(XD_4)_z$,
15 $(A_{1-a}M''_a)_xM'_y(DXD_4)_z$, or $(A_{1-a}M''_a)_xM'_y(X_2D_7)_z$, having a conductivity at 27° C of at
least about 10^{-8} S/cm, wherein A is at least one of an alkali metal or hydrogen, M' is a
first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, boron,
aluminum, silicon, vanadium, molybdenum and tungsten, M'' any of a Group IIA, IIIA,
IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least one of
20 oxygen, nitrogen, carbon, or a halogen, $0.0001 < a \leq 0.1$, and x, y, and z are greater than
zero and have values such that (1-a)x plus the quantity ax times the formal valence or
valences of M'' plus y times the formal valence or valences of M' is equal to z times the
formal valence of the XD_4 , X_2D_7 or DXD_4 group.

3. A compound comprising a composition $(A_{b-a}M''_a)_xM'_y(XD_4)_z$,
25 $(A_{b-a}M''_a)_xM'_y(DXD_4)_z$, or $(A_{b-a}M''_a)_xM'_y(X_2D_7)_z$, having a conductivity at 27° C of at
least about 10^{-8} S/cm, wherein A is at least one of an alkali metal or hydrogen, M' is a
first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, boron,
aluminum, silicon, vanadium, molybdenum and tungsten, M'' any of a Group IIA, IIIA,
30 IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least one of
oxygen, nitrogen, carbon, or a halogen, $0.0001 < a \leq 0.1$, $a \leq b \leq 1$, and x, y, and z are
greater than zero and have values such that (b-a)x plus the quantity ax times the formal

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valence or valences of M'' plus y times the formal valence or valences of M' is equal to z times the formal valence of the XD_4 , X_2D_7 or DXD_4 group.

4. A compound comprising a composition $A_x(M'_{1-a}M''_a)_y(XD_4)_z$,
 $A_x(M'_{1-a}M''_a)_y(DXD_4)_z$, or $A_x(M'_{1-a}M''_a)_y(X_2D_7)_z$, having a specific surface area of at
 5 least $15 \text{ m}^2/\text{g}$, wherein A is at least one of an alkali metal or hydrogen, M' is a first-row
 transition metal, X is at least one of phosphorus, sulfur, arsenic, boron, aluminum,
 silicon, vanadium, molybdenum and tungsten, M'' is any of a Group IIA, IIIA, IVA, VA,
 VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least one of oxygen,
 10 nitrogen, carbon, or a halogen, $0.0001 < a \leq 0.1$, and x is equal to or greater than 0, y and
 z are greater than 0 and have values such that x , plus $y(1-a)$ times a formal valence or
 valences of M' , plus ya times a formal valence or valence of M'' , is equal to z times a
 formal valence of the XD_4 , X_2D_7 , or DXD_4 group.
- 15 5. A compound comprising a composition $(A_{1-a}M''_a)_xM'_y(XD_4)_z$,
 $(A_{1-a}M''_a)_xM'_y(DXD_4)_z$, or $(A_{1-a}M''_a)_xM'_y(X_2D_7)_z$, having a specific surface area of at
 least $15 \text{ m}^2/\text{g}$, wherein A is at least one of an alkali metal or hydrogen, M' is a first-row
 transition metal, X is at least one of phosphorus, sulfur, arsenic, boron, aluminum,
 silicon, vanadium, molybdenum and tungsten, M'' any of a Group IIA, IIIA, IVA, VA,
 20 VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least one of oxygen,
 nitrogen, carbon, or a halogen, $0.0001 < a \leq 0.1$, and x , y , and z are greater than zero and
 have values such that $(1-a)x$ plus the quantity ax times the formal valence or valences of
 M'' plus y times the formal valence or valences of M' is equal to z times the formal
 valence of the XD_4 , X_2D_7 or DXD_4 group.
- 25 6. A compound comprising a composition $(A_{b-a}M''_a)_xM'_y(XD_4)_z$,
 $(A_{b-a}M''_a)_xM'_y(DXD_4)_z$, or $(A_{b-a}M''_a)_xM'_y(X_2D_7)_z$, having a specific surface area of at
 least $15 \text{ m}^2/\text{g}$, wherein A is at least one of an alkali metal or hydrogen, M' is a first-row
 transition metal, X is at least one of phosphorus, sulfur, arsenic, boron, aluminum,
 30 silicon, vanadium, molybdenum and tungsten, M'' any of a Group IIA, IIIA, IVA, VA,
 VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least one of oxygen,
 nitrogen, carbon, or a halogen, $0.0001 < a \leq 0.1$, $a \leq b \leq 1$, and x , y , and z are greater

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than zero and have values such that $(b-a)x$ plus the quantity ax times the formal valence or valences of M'' plus y times the formal valence or valences of M' is equal to z times the formal valence of the XD_4 , X_2D_7 or DXD_4 group.

- 5 7. A compound comprising a composition $A_x(M'_{1-a}M''_a)_y(XD_4)_z$, $A_x(M'_{1-a}M''_a)_y(DXD_4)_z$, or $A_x(M'_{1-a}M''_a)_y(X_2D_7)_z$, wherein A is at least one of an alkali metal or hydrogen, M' is a first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, boron, aluminum, silicon, vanadium, molybdenum and tungsten, M'' is any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least one of oxygen, nitrogen, carbon, or a halogen, $0.0001 < a \leq 0.1$, and x is equal to or greater than 0, y and z are greater than 0 and have values such that x , plus $y(1-a)$ times a formal valence or valences of M' , plus ya times a formal valence or valence of M'' , is equal to z times a formal valence of the XD_4 , X_2D_7 , or DXD_4 group, crystallizing in an ordered or partially disordered structure of the olivine (A_xMXO_4),
 - 15 NASICON ($A_x(M', M'')_2(XO_4)_3$), $VOPO_4$, $LiFe(P_2O_7)$ or $Fe_4(P_2O_7)_3$ structure-types, and additionally having a molar concentration of the metals ($M' + M''$) relative to the concentration of the elements X that exceeds the ideal stoichiometric ratio y/z of the prototype compounds by at least 0.0001.
- 20 8. A compound comprising a composition $(A_{1-a}M''_a)_xM'_y(XD_4)_z$, $(A_{1-a}M''_a)_xM'_y(DXD_4)_z$, or $(A_{1-a}M''_a)_xM'_y(X_2D_7)_z$, wherein A is at least one of an alkali metal or hydrogen, M' is a first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, boron, aluminum, silicon, vanadium, molybdenum and tungsten, M'' any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least one of oxygen, nitrogen, carbon, or a halogen, $0.0001 < a \leq 0.1$, and x , y , and z are greater than zero and have values such that $(1-a)x$ plus the quantity ax times the formal valence or valences of M'' plus y times the formal valence or valences of M' is equal to z times the formal valence of the XD_4 , X_2D_7 or DXD_4 group, crystallizing in an ordered or partially disordered structure of the olivine (A_xMXO_4),
 - 25
 - 30 NASICON ($A_x(M', M'')_2(XO_4)_3$), $VOPO_4$, $LiFe(P_2O_7)$ or $Fe_4(P_2O_7)_3$ structure-types, and additionally having a molar concentration of the metals ($M' + M''$) relative to the

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concentration of the elements X that exceeds the ideal stoichiometric ratio y/z of the prototype compounds by at least 0.0001.

9. A compound comprising a composition $(A_{b-a}M''_a)_xM'_y(XD_4)_z$,
 5 $(A_{b-a}M''_a)_xM'_y(DXD_4)_z$, or $(A_{b-a}M''_a)_xM'_y(X_2D_7)_z$, wherein A is at least one of an alkali metal or hydrogen, M' is a first-row transition metal, X is at least one of phosphorus, sulfur, arsenic, boron, aluminum, silicon, vanadium, molybdenum and tungsten, M'' any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal, D is at least one of oxygen, nitrogen, carbon, or a halogen, $0.0001 < a \leq 0.1$, $a \leq b$
 10 ≤ 1 , and x, y, and z are greater than zero and have values such that $(b-a)x$ plus the quantity ax times the formal valence or valences of M'' plus y times the formal valence or valences of M' is equal to z times the formal valence of the XD_4 , X_2D_7 or DXD_4 group, crystallizing in an ordered or partially disordered structure of the olivine (A_xMXO_4) , NASICON $(A_x(M',M'')_2(XO_4)_3)$, $VOPO_4$, $LiFe(P_2O_7)$ or $Fe_4(P_2O_7)_3$
 15 structure-types, and additionally having a molar concentration of the metals $(M' + M'')$ relative to the concentration of the elements X that exceeds the ideal stoichiometric ratio y/z of the prototype compounds by at least 0.0001.
10. A compound as in any of claims 1-9, wherein the compound can intercalate at
 20 least one of an alkali or hydrogen.
11. A compound as in any of claims 1-9, wherein M'' has a formal valence greater than 1+ as an ion in the compound.
- 25 12. A compound as in any of claims 1-9, wherein M'' is any of aluminum, titanium, zirconium, niobium, tantalum, tungsten, and magnesium.
13. A compound as in any of claims 1-9, wherein A is lithium.
- 30 14. A compound as in any of claims 1-9, wherein X is phosphorus.
15. A compound as in any of claims 1-9, wherein D is oxygen.

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16. A compound as in any of claims 1-9, wherein M' is any of iron, vanadium, chromium, manganese, cobalt or nickel.
- 5 17. A compound as in any of claims 1-9, wherein M' is Fe²⁺.
18. A compound as in any of claims 1-9, wherein at least one of M' and M'' has an ionic radius less than the ionic radius of Fe²⁺.
- 10 19. A compound as in any of claims 1-9, wherein the compound is substantially free of silicon.
20. A compound as in any of claims 1-9, wherein the compound has a crystalline structure in which at least one of the M' or M'' atoms occupy lattice sites coordinated by
15 anion polyhedra, said polyhedra forming a continuous network through the structure by sharing at least one of vertices, corners, edges, or faces.
21. A compound as in claim 20, wherein the polyhedra of the continuous network are filled with transition-metals.
- 20 22. A compound as in any of claims 20-21, wherein the polyhedral units are octahedra or distorted octahedra.
23. A compound as in any of claims 20-22, wherein polyhedral units share corners
25 and edges with other polyhedral units containing M' or M''.
24. A compound as in any of claims 1-9, wherein the compound is an n-type conductor.
- 30 25. A compound as in any of claims 1-9, wherein the compound comprises a mixture of an n-type conductor and a p-type conductor.

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26. A compound as in any of claims 1-9, wherein the compound is a p-type conductor.
27. A compound as in any of claims 1-9, wherein A is lithium and during preparation
5 or use the compound is substantially fully delithiated.
28. A compound as in any of claims 1-9, wherein the compound is a p-type conductor when substantially fully lithiated and an n-type conductor when substantially fully delithiated.
- 10 29. A compound as in any of claims 1-9, wherein the compound, upon delithiation, undergoes phase-separation into a substantially lithiated compound and a substantially delithiated compound, each of which have an electronic conductivity of at least 10^{-6} S/cm.
- 15 30. A compound as in any of claims 1-9, wherein x has a value between zero and about 1, y is about 1, and z is about 1.
31. A compound as in any of claims 1-9, wherein x has a value between zero and
20 about 1, and y is about 1.
32. A compound as in any of claims 1-9, wherein x has a value between zero and about 5, y is about 2, and z is about 3.
- 25 33. A compound as in any of claims 1-9, wherein x has a value between zero and about 2, y is about 1, and z is about 1.
34. A compound as in any of claims 1-9, wherein x has a value between zero and about 4, y is about 4, and z is about 3.
- 30 35. A compound as in any of claims 1-9, wherein $0 < x/(x+y+z) \leq 2/3$.

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36. A compound as in any of claims 1-9, wherein the compound has at least one of an ordered or partially disordered structure of the olivine (A_xMXO_4), NASICON ($A_x(M',M'')_2(XO_4)_3$), $VOPO_4$, $LiFe(P_2O_7)$ or $Fe_4(P_2O_7)_3$ structure-types.
- 5 37. A compound as in any of claims 1-9, wherein the compound is $LiFePO_4$ containing additional metals M'' .
38. A compound as in any of claims 1-9, wherein the compound has an olivine structure and contains in crystalline solid solution, amongst the metals M' and M'' ,
10 simultaneously metal ions of at least one type that is oxidizable and another that is reducible at 23°C.
39. A compound as in any of claims 1-9, wherein the compound has an olivine structure and contains in crystalline solid solution, amongst the metals M' and M'' ,
15 simultaneously the metal ions Fe^{2+} and Fe^{3+} , Mn^{2+} and Mn^{3+} , Co^{2+} and Co^{3+} , Ni^{2+} and Ni^{3+} , V^{2+} and V^{3+} , or Cr^{2+} and Cr^{3+} , with the ion of lesser concentration being at least 10 parts per million of the sum of the two ion concentrations.
40. A compound as in any of claims 1-9, wherein the compound has an olivine
20 structure, M' includes Fe, and at least one of M' and M'' has an ionic radius less than the ionic radius of Fe^{2+} .
41. A compound as in any of claims 1-9, wherein the compound has an olivine structure, and M'' includes at least one metal with ionic radius less than the average ionic
25 radius of the M' ions.
42. A compound as in any of claims 1-9, wherein the compound has an olivine structure with a crystalline solid solution of formula $A_xvac_y(M'_{1-a}M''_a)XO_4$, $A_{x-a-y}M''_avac_yM'XO_4$, $A_x(M'_{1-a-y}M''_avac_y)XO_4$ or $A_{x-a}M''_aM'_{1-y}vac_yXO_4$, wherein vac
30 represents a vacancy in any of an M1 and M2 site of the primary crystallites.

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43. A compound as in any of claims 1-9, wherein said compound has the ordered olivine structure type and A is lithium and is substituted onto a M2 site of a crystal of the composition at a concentration of at least about 10^{18} per cubic centimeter.
- 5 44. A compound as in any of claims 1-9, wherein said compound has the ordered olivine structure type and A is lithium and x and a are selected such that lithium can substitute into an M2 site of a crystal of the composition as an acceptor defect.
45. A compound as in any of claims 1-9, wherein the composition is any of
 10 $\text{Li}_x(\text{M}'_{1-a}\text{M}''_a)\text{PO}_4$, $\text{Li}_x\text{M}''_a\text{M}'\text{PO}_4$, $\text{Li}_x(\text{M}'_{1-a-y}\text{M}''_a\text{Li}_y)\text{PO}_4$, or $\text{Li}_{x-a}\text{M}''_a\text{M}'_{1-y}\text{Li}_y\text{PO}_4$.
46. A compound as in any of claims 1-9, wherein the composition is any of
 $\text{Li}_x(\text{Fe}_{1-a}\text{M}''_a)\text{PO}_4$, $\text{Li}_x\text{M}''_a\text{FePO}_4$, $\text{Li}_x(\text{Fe}_{1-a-y}\text{M}''_a\text{Li}_y)\text{PO}_4$, or $\text{Li}_{x-a}\text{M}''_a\text{Fe}_{1-y}\text{Li}_y\text{PO}_4$.
- 15 47. A compound as in any of claims 1-9, wherein the composition is $\text{Li}_x\text{vac}_{1-x}(\text{M}'_{1-a}\text{M}''_a)\text{PO}_4$, $\text{Li}_x\text{M}''_a\text{vac}_{1-a-y}\text{M}'\text{PO}_4$, $\text{Li}_x(\text{M}'_{1-a-y}\text{M}''_a\text{vac}_y)\text{PO}_4$ or $\text{Li}_{x-a}\text{M}''_a\text{M}'_{1-y}\text{vac}_y\text{PO}_4$, wherein vac represents a vacancy in a structure of the compound.
48. A compound as in any of claims 1-9, wherein the composition is $\text{Li}_x\text{vac}_{1-x}(\text{Fe}_{1-a}\text{M}''_a)\text{PO}_4$, $\text{Li}_x\text{M}''_a\text{vac}_{1-a-y}\text{FePO}_4$, $\text{Li}_x(\text{Fe}_{1-a-y}\text{M}''_a\text{vac}_y)\text{PO}_4$ or $\text{Li}_{x-a}\text{M}''_a\text{Fe}_{1-y}\text{vac}_y\text{PO}_4$,
 20 wherein vac represents a vacancy in a structure of the compound.
49. A compound as in any of claims 1-9, wherein the compound has an olivine structure and at least a portion of A occupies a M1 site.
- 25 50. A compound as in any of claims 1-9, wherein M'' is substantially in solid solution in a crystal structure of the compound.
51. A compound as in any of claims 1-9, wherein M'' is partially in solid solution in a
 30 crystal structure of the compound at a concentration of at least 0.01 atom % relative to the concentration of M', the balance appearing as an additional phase.
52. A compound as in claim 51, wherein the concentration is at least 0.02 mole %.

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53. A compound as in claim 51, wherein the concentration is at least 0.05 mole %.
54. A compound as in claim 51, wherein the concentration is at least 0.1 mole %.
- 5 55. A compound as in any of claims 1-9, wherein the compound comprises doped LiFePO_4 in an olivine structure.
56. A compound as in any of claims 1-9, wherein the compound forms primary
10 crystallites, at least 50 % of which have a smallest dimension less than 500 nm.
57. A compound as in any of claims 1-9, wherein the smallest dimension is less than 200 nm.
- 15 58. A compound as in any of claims 1-9, wherein the smallest dimension is less than 100 nm.
59. A compound as in any of claims 1-9, wherein the smallest dimension is less than 50 nm.
- 20 60. A compound as in any of claims 1-9, wherein the smallest dimension is less than 20 nm.
61. A compound as in any of claims 1-9, wherein the smallest dimension is less than
25 10 nm.
62. A compound as in any of claims 1-9, wherein the primary crystallites form an interconnected porous network
- 30 63. A compound as in any of claims 1-9, wherein at least about 25 % of the surface area of the primary crystallites is available for contact with an electrolyte.

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64. A compound as in any of claims 1-9, wherein at least about 50 % of the surface area of the primary crystallites is in contact with an electrolyte.
65. A compound as in any of claims 1-9, wherein the compound has a specific surface area of at least about 10 m²/g.
66. A compound as in any of claims 1-9, wherein the specific surface area is at least about 20 m²/g.
67. A compound as in any of claims 1-9, wherein the specific surface area is at least about 30 m²/g.
68. A compound as in any of claims 1-9, wherein the specific surface area is at least about 40 m²/g.
69. A compound as in any of claims 1-9, wherein the specific surface area is at least about 50 m²/g.
70. A compound as in any of claims 1-9, wherein the conductivity is at least about 10⁻⁷ S/cm.
71. A compound as in any of claims 1-9, wherein the conductivity is at least about 10⁻⁶ S/cm.
72. A compound as in any of claims 1-9, wherein the conductivity is at least about 10⁻⁵ S/cm.
73. A compound as in any of claims 1-9, wherein the conductivity is at least about 10⁻⁴ S/cm.
74. A compound as in any of claims 1-9, wherein the conductivity is at least about 10⁻³ S/cm.

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75. A compound as in any of claims 1-9, wherein the conductivity is at least about 10^{-2} S/cm.
76. A compound as in any of claims 1-9, further comprising less than about 15 weight percent of a conductivity-enhancing additive based on the weight of the composition.
77. A compound as in claim 76, wherein the conductivity-enhancing additive is present in an amount of less than about 10 weight percent.
78. A compound as in claim 76, wherein the conductivity-enhancing additive is present in an amount of less than about 7 weight percent.
79. A compound as in claim 76, wherein the conductivity-enhancing additive is present in an amount of less than about 5 weight percent.
80. A compound as in claim 76, wherein the conductivity-enhancing additive is present in an amount of less than about 3 weight percent.
81. A compound as in claim 76, wherein the conductivity-enhancing additive is present in an amount of less than about 2 weight percent.
82. A compound as in claim 76, wherein the conductivity-enhancing additive is present in an amount of less than about 1 weight percent.
83. A compound as in claim 76, wherein the conductivity-enhancing additive comprises carbon.
84. A compound as in any of claims 1-9, wherein the compound forms at least part of an electrode in an electrochemical device.
85. A compound as in any of claims 1-9, wherein the electrochemical device is a fuel cell.

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86. A compound as in any of claims 1-9, wherein the compound is a mixed proton conducting and electronically conducting material.
- 5 87. A compound as in any of claims 1-9, wherein the compound is a gas separation membrane comprising a mixed proton conducting and electronically conducting material.
88. A compound as in any of claims 1-9, wherein the compound is a gas
10 separation membrane comprising a mixed proton conducting and electronically conducting material comprising LiFePO_4 .
89. A compound as in any of claims 1-9 formed by mixing an alkali metal or hydrogen salt, a first-row transition metal compound, a salt of at least one of phosphorus,
15 sulfur, arsenic, molybdenum and tungsten, and an ethoxide or methoxide of any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal; milling the mixture; and heat treating the mixture at a first temperature sufficient to form at least one of an olivine, NASICON, VOPO_4 , $\text{LiFe}(\text{P}_2\text{O}_7)$ or $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ structure.
- 20 90. A method of forming a compound, comprising:
mixing an alkali metal or hydrogen salt, a first-row transition metal salt, a salt of at least one of phosphorus, sulfur, arsenic, silicon, aluminum, boron, vanadium, molybdenum and tungsten, and a salt of any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal;
25 milling the mixture; and
heat treating the mixture at a temperature between 300-900°C.
91. A method as in claim 90, wherein the alkali metal salt is a metal carbonate.
92. A method as in claim 90, wherein the alkali metal salt is lithium carbonate.
- 30 93. A method as in claim 90, wherein the alkali metal salt is LiPO_3 .

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94. A method as in claim 90, wherein the salt of the first-row transition metal is a metal oxalate.
95. A method as in claim 90, wherein the salt of the first-row transition metal is a metal acetate.
- 5 96. A method as in claim 90, wherein the salt of the first-row transition metal is a metal oxide.
97. A method as in claim 90, wherein the salt of the first-row transition metal is iron oxalate.
98. A method as in claim 90, wherein the salt of the first-row transition metal is iron
10 acetate.
99. A method as in claim 90, wherein the salt of the first-row transition metal is iron oxide.
100. A method as in claim 90, wherein the salt of at least one of phosphorus, sulfur, arsenic, silicon, aluminum, boron, vanadium, molybdenum and tungsten, is ammonium
15 phosphate.
101. A method as in claim 90, wherein the salt of at least one of phosphorus, sulfur, arsenic, silicon, aluminum, boron, vanadium, molybdenum and tungsten, is LiPO_3 .
102. A method as in claim 90, wherein the salt of at least one of phosphorus, sulfur, arsenic, silicon, aluminum, boron, vanadium, molybdenum and tungsten, is P_2O_5 .
- 20 103. A method as in claim 90, wherein the salt of at least one of phosphorus, sulfur, arsenic, silicon, aluminum, boron, vanadium, molybdenum and tungsten, is phosphoric acid.
104. A method as in claim 90, wherein the salt of any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal is a metal alkoxide.
- 25 105. A method as in claim 90, wherein the salt of any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal is a metal oxide.

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106. A method as in claim 90, wherein the salt of any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal is a metal acetate.
107. A method as in claim 90, wherein the salt of any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal is a metal nitrate.
- 5 108. A method as in claim 90, wherein the salts comprise lithium carbonate, iron oxalate, ammonium phosphate, and an alkoxide of any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal.
109. A method as in claim 90, wherein the salts comprise lithium carbonate, iron oxalate, ammonium phosphate, and an alkoxide of any of magnesium, aluminum, iron,
10 manganese, titanium, zirconium, niobium, tantalum, or tungsten.
110. A method as in claim 90, wherein the salts comprise lithium carbonate, iron oxalate, ammonium phosphate, and an oxide of any of magnesium, aluminum, iron, titanium, zirconium, niobium, tantalum, or tungsten.
111. A method as in claim 90, wherein the salts comprise LiPO_3 , FeO , and an alkoxide
15 of any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal.
112. A method as in claim 90, wherein the salts comprise LiPO_3 , FeO , and an oxide of any of a Group IIA, IIIA, IVA, VA, VIA, VIIA, VIIIA, IB, IIB, IIIB, IVB, VB, and VIB metal.
- 20 113. A method as in claim 90, wherein the salts comprise LiPO_3 , FeO , and an alkoxide of any of magnesium, aluminum, iron, manganese, titanium, zirconium, niobium, tantalum, or tungsten.
114. A method as in claim 90, wherein mixing is performed while the mixture is under a nonreactive atmosphere.
- 25 115. A method as in claim 90, wherein heat-treating is performed while the mixture is under a gaseous atmosphere with an oxygen partial pressure of less than about 10^{-4} atmospheres.

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116. A method as in claim 90, wherein heat-treating is performed while the mixture is under a gaseous atmosphere with an oxygen partial pressure of less than about 10^{-5} atmospheres.
117. A method as in claim 90, wherein heat-treating is performed while the mixture is
5 under a gaseous atmosphere with an oxygen partial pressure of less than about 10^{-6} atmospheres.
118. A method as in claim 90, wherein heat-treating is performed in a gaseous atmosphere that is substantially nitrogen gas.
119. A method as in claim 90, wherein heat-treating is performed in a gaseous
10 atmosphere that is substantially argon gas.
120. A method as in claim 90, wherein heat-treating is performed in a gaseous atmosphere that is substantially hydrogen gas.
121. A method as in claim 90, wherein heat-treating is performed in a gaseous atmosphere that is substantially a mixture of nitrogen and hydrogen gas.
- 15 122. A method as in claim 90, wherein heat-treating is performed in a gaseous atmosphere that is substantially a mixture of carbon monoxide and carbon dioxide gas.
123. A method as in claim 90, wherein heat-treating is performed in a gaseous atmosphere that is substantially nitrogen gas.
124. A method as in claim 90, further comprising heat treatment at two temperatures,
20 the second heat treatment being at a temperature higher the first temperature.
125. A method as in claim 90, further comprising heat treatment at two temperatures, the first temperature being from 300-400°C and the second temperature being from 500-900°C.
126. A method of doping a material to form a lithium or hydrogen storage compound,
25 comprising:

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selecting a starting material to be doped, in conjunction with selection of milling equipment comprising a dopant for doping the starting material at a predetermined level of dopant;

milling the starting material in the milling equipment; and

5 recovering from the milling step a material suitable for forming a lithium or hydrogen storage compound comprising the starting material doped with the dopant at the predetermined level.

127. A method as in claim 126, wherein the lithium or hydrogen storage compound is
10 any one of the compounds of claims 1-9.

128. A method as in claim 126, wherein the dopant added from the milling equipment is at least one of zirconium, aluminum, iron, carbon, or fluorine.

15 129. A method as in claim 126, wherein the dopant comprises at least zirconium and the milling equipment comprises zirconia milling media or containers.

130. A method as in claim 126, wherein the dopant comprises at least aluminum and the milling equipment comprises aluminum oxide milling media or containers.

20

131. A method as in claim 126, wherein the dopant comprises at least iron and the milling equipment comprises iron or steel milling media or containers.

132. A method as in claim 126, wherein the dopant comprises at least carbon and the
25 milling equipment comprises polymer milling media or containers.

133. A method as in claim 126, wherein said milling equipment includes at least one of polypropylene-bearing, polystyrene-bearing, or polytetrafluoroethylene-bearing milling media or milling containers.

30

134. A method as in claim 126, wherein the dopant comprises at least fluorine and the milling equipment comprises fluoropolymer milling media or containers.

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135. An electrode comprising a compound of any one of claims 1-9 and having a material energy density that while:

charging or discharging at a rate ≥ 30 mA per g of storage compound, is greater than 350 Wh/kg, or

5 charging or discharging at a rate ≥ 150 mA per g of storage compound, is greater than 280 Wh/kg, or

charging or discharging at a rate ≥ 300 mA per g of storage compound, is greater than 270 Wh/kg, or

10 charging or discharging at a rate ≥ 750 mA per g of storage compound, is greater than 250 Wh/kg, or

charging or discharging at a rate ≥ 1.5 A per g of storage compound, is greater than 180 Wh/kg, or

charging or discharging at a rate ≥ 3 A per g of storage compound, is greater than 40 Wh/kg, or

15 charging or discharging at a rate ≥ 4.5 A per g of storage compound, is greater than 10 Wh/kg.

136. An electrode as in claim 135, having a material energy density that while:

20 charging or discharging at a rate ≥ 30 mA per g of storage compound, is greater than 420 Wh/kg, or

charging or discharging at a rate ≥ 150 mA per g of storage compound, is greater than 400 Wh/kg, or

charging or discharging at a rate ≥ 300 mA per g of storage compound, is greater than 370 Wh/kg, or

25 charging or discharging at a rate ≥ 750 mA per g of storage compound, is greater than 350 Wh/kg, or

charging or discharging at a rate ≥ 1.5 A per g of storage compound, is greater than 270 Wh/kg, or

30 charging or discharging at a rate ≥ 3 A per g of storage compound, is greater than 150 Wh/kg, or

charging or discharging at a rate ≥ 4.5 A per g of storage compound, is greater than 80 Wh/kg, or

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- charging or discharging at a rate ≥ 6 A per g of storage compound, is greater than 35 Wh/kg, or
charging or discharging at a rate ≥ 7.5 A per g of storage compound, is greater than 50 Wh/kg, or
5 charging or discharging at a rate ≥ 15 A per g of storage compound, is greater than 10 Wh/kg,
137. An electrode as in claim 135, having a material energy density that while:
charging or discharging at a rate ≥ 30 mA per g of storage compound, is greater
10 than 475 Wh/kg, or
charging or discharging at a rate ≥ 150 mA per g of storage compound, is greater than 450 Wh/kg, or
charging or discharging at a rate ≥ 300 mA per g of storage compound, is greater than 430 Wh/kg, or
15 charging or discharging at a rate ≥ 750 mA per g of storage compound, is greater than 390 Wh/kg, or
charging or discharging at a rate ≥ 1.5 A per g of storage compound, is greater than 350 Wh/kg, or
charging or discharging at a rate ≥ 3 A per g of storage compound, is greater than
20 300 Wh/kg, or
charging or discharging at a rate ≥ 4.5 A per g of storage compound, is greater than 250 Wh/kg, or
charging or discharging at a rate ≥ 7.5 A per g of storage compound, is greater than 150 Wh/kg, or
25 charging or discharging at a rate ≥ 11 A per g of storage compound, is greater than 50 Wh/kg, or
charging or discharging at a rate ≥ 15 A per g of storage compound, is greater than 30 Wh/kg.
- 30 138. An electrode comprising a lithium storage compound other than one of ordered or partially ordered rocksalt crystal structure type, or spinel crystal structure type, or

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vanadium oxide or manganese oxide, the electrode having a material energy density that while:

- charging or discharging at a rate ≥ 800 mA per g of storage compound, is greater than 250 Wh/kg, or
- 5 charging or discharging at a rate ≥ 1.5 A per g of storage compound, is greater than 180 Wh/kg, or
- charging or discharging at a rate ≥ 3 A per g of storage compound, is greater than 40 Wh/kg, or
- charging or discharging at a rate ≥ 4.5 A per g of storage compound, is greater than 10 Wh/kg.
- 10
139. An electrode as in claim 138, having a material energy density that while:
- charging or discharging at a rate ≥ 800 mA per g of storage compound, is greater than 350 Wh/kg, or
- 15 charging or discharging at a rate ≥ 1.5 A per g of storage compound, is greater than 270 Wh/kg, or
- charging or discharging at a rate ≥ 3 A per g of storage compound, is greater than 150 Wh/kg, or
- charging or discharging at a rate ≥ 4.5 A per g of storage compound, is greater than 80 Wh/kg, or
- 20 charging or discharging at a rate ≥ 6 A per g of storage compound, is greater than 35 Wh/kg, or
- charging or discharging at a rate ≥ 7.5 A per g of storage compound, is greater than 50 Wh/kg, or
- 25 charging or discharging at a rate ≥ 15 A per g of storage compound, is greater than 10 Wh/kg,
140. An electrode as in claim 138, having a material energy density that while:
- charging or discharging at a rate ≥ 800 mA per g of storage compound, is greater than 390 Wh/kg, or
- 30 charging or discharging at a rate ≥ 1.5 A per g of storage compound, is greater than 350 Wh/kg, or

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- charging or discharging at a rate ≥ 3 A per g of storage compound, is greater than
300 Wh/kg, or
charging or discharging at a rate ≥ 4.5 A per g of storage compound, is greater
than 250 Wh/kg, or
5 charging or discharging at a rate ≥ 7.5 A per g of storage compound, is greater
than 150 Wh/kg, or
charging or discharging at a rate ≥ 11 A per g of storage compound, is greater
than 50 Wh/kg, or
charging or discharging at a rate ≥ 15 A per g of storage compound, is greater
10 than 30 Wh/kg.
141. An electrode comprising a compound as in any one of claims 1-9.
142. An electrode as in claim 141, wherein the electrode comprises a sheet or a mesh
15 coated or impregnated with the storage compound.
143. An electrode as in claim 141, wherein the electrode comprises a metal foil coated
one or both sides with the storage compound.
- 20 144. An electrode as in claim 141, wherein the electrode is a sheet or mesh of
electronically conductive material coated with a loading of at least 4 mg of said storage
compound per square centimeter of projected area of the sheet or mesh.
145. An electrode as in claim 141, wherein said electrode is a sheet or mesh of
25 electronically conductive material coated with a loading of at least 8 mg of said storage
compound per square centimeter of projected area of the sheet or mesh.
146. An electrode as in claim 141, wherein said electrode is a sheet or mesh of
electronically conductive material coated with a loading of at least 10 mg of said storage
30 compound per square centimeter of projected area of the sheet or mesh.

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147. An electrode as in claim 141, wherein said electrode is a sheet or mesh of electronically conductive material coated with a loading of at least 14 mg of said storage compound per square centimeter of projected area of the sheet or mesh.
- 5 148. An electrode as in claim 141, wherein said electrode is a sheet or mesh of electronically conductive material coated with a loading of at least 20 mg of said storage compound per square centimeter of projected area of the sheet or mesh.
- 10 149. An electrode as in claim 141, wherein said electrode is a sheet or mesh of electronically conductive material coated with said storage material and has a total thickness of at least 20 micrometers.
- 15 150. An electrode as in claim 141, wherein said electrode is a sheet or mesh of electronically conductive material coated with said storage material and has a total thickness of at least 40 micrometers.
- 20 151. An electrode as in claim 141, wherein said electrode is a sheet or mesh of electronically conductive material coated with said storage material and has a total thickness of at least 60 micrometers.
- 25 152. An electrode as in claim 141, wherein said electrode is a sheet or mesh of electronically conductive material coated with said storage material and has a total thickness of at least 80 micrometers.
- 30 153. An electrode as in claim 141, wherein said electrode is a sheet or mesh of electronically conductive material coated with said storage material and has a total thickness of at least 100 micrometers.
154. An electrode as in claim 141, wherein said electrode is a sheet or mesh of electronically conductive material coated with said storage material and has a total thickness of at least 150 micrometers.

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155. An electrode as in claim 141, wherein said electrode is a sheet or mesh of electronically conductive material coated with said storage material and has a total thickness of at least 200 micrometers.
- 5 156. A storage battery cell comprising:
a positive electrode;
a negative electrode; and
a separator positioned between the positive electrode and the negative electrode.
wherein at least one of the positive electrode or negative electrode comprises the
10 compound of claim 1.
157. A storage battery cell as in claim 156 wherein the cell is a disposable battery cell.
158. A storage battery cell as in claim 156 wherein the cell is a rechargeable battery
15 cell.
159. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge an energy of at least 0.25 Wh.
- 20 160. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge an energy of at least 1 Wh.
161. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge an energy of at least 5 Wh.
- 25 162. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge an energy of at least 10 Wh.
163. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge an
30 energy of at least 20 Wh.
164. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge an energy of at least 30 Wh.

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165. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge an energy of at least 40 Wh.

5 166. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge an energy of at least 50 Wh.

167. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge an energy of at least 100 Wh.

10

168. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge a gravimetric energy density of at least 30 Wh/kg or a volumetric energy density of at least 100 Wh/liter.

15 169. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge a gravimetric energy density of at least 50 Wh/kg or a volumetric energy density of at least 200 Wh/liter.

20 170. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge a gravimetric energy density of at least 90 Wh/kg or a volumetric energy density of at least 300 Wh/liter.

25 171. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge a gravimetric power density of at least 100 W/kg or a volumetric power density of at least 350 W/liter.

172. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge a gravimetric power density of at least 500 W/kg or a volumetric power density of at least 500 W/liter.

30

173. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge a gravimetric power density of at least 1000 W/kg or a volumetric power density of at least 1000 W/liter.

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174. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge a gravimetric power density of at least 2000 W/kg or a volumetric power density of at least 2000 Wh/liter.
- 5
175. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge a gravimetric energy density of at least:
- 30 Wh/kg at a power density of at least 500 W/kg, or
 - 20 Wh/kg at a power density of at least 1000 W/kg, or
 - 10 Wh/kg at a power density of at least 1500 W/kg, or
 - 5 Wh/kg at a power density of at least 2000 W/kg, or
 - 2 Wh/kg at a power density of at least 2500 W/kg, or
 - 1 Wh/kg at a power density of at least 3000 W/kg.
- 10
176. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge a gravimetric energy density of at least:
- 50 Wh/kg at a power density of at least 500 W/kg, or
 - 40 Wh/kg at a power density of at least 1000 W/kg, or
 - 20 Wh/kg at a power density of at least 2000 W/kg, or
 - 10 Wh/kg at a power density of at least 3000 W/kg, or
 - 4 Wh/kg at a power density of at least 4000 W/kg, or
 - 1 Wh/kg at a power density of at least 5000 W/kg.
- 15
177. A storage battery cell as in claim 156 wherein the cell exhibits upon discharge a gravimetric energy density of at least:
- 80 Wh/kg at a power density of at least 1000 W/kg, or
 - 70 Wh/kg at a power density of at least 2000 W/kg, or
 - 60 Wh/kg at a power density of at least 3000 W/kg, or
 - 55 Wh/kg at a power density of at least 4000 W/kg, or
 - 50 Wh/kg at a power density of at least 5000 W/kg, or
 - 30 Wh/kg at a power density of at least 6000 W/kg, or
 - 10 Wh/kg at a power density of at least 8000 W/kg.
- 20
- 25
- 30

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178. A storage battery cell as in claim 156, wherein the lithium storage compound is any other than a compound with an ordered or partially disordered rocksalt or spinel structure type, or vanadium oxide, or manganese oxide.

FIG. 1

0.1% Ti/600°C/Ar/24 h

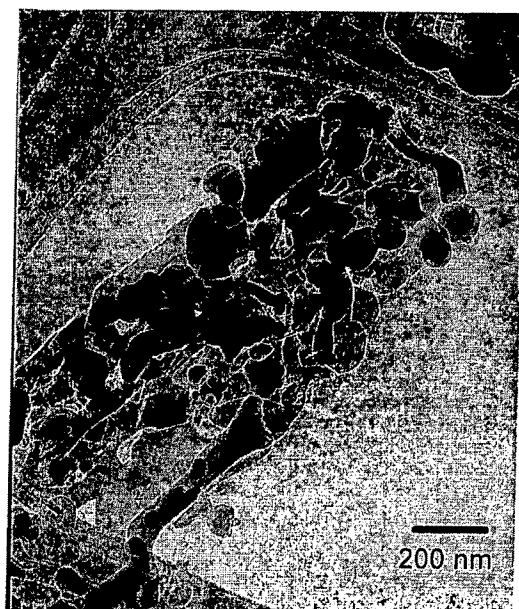


FIG. 2

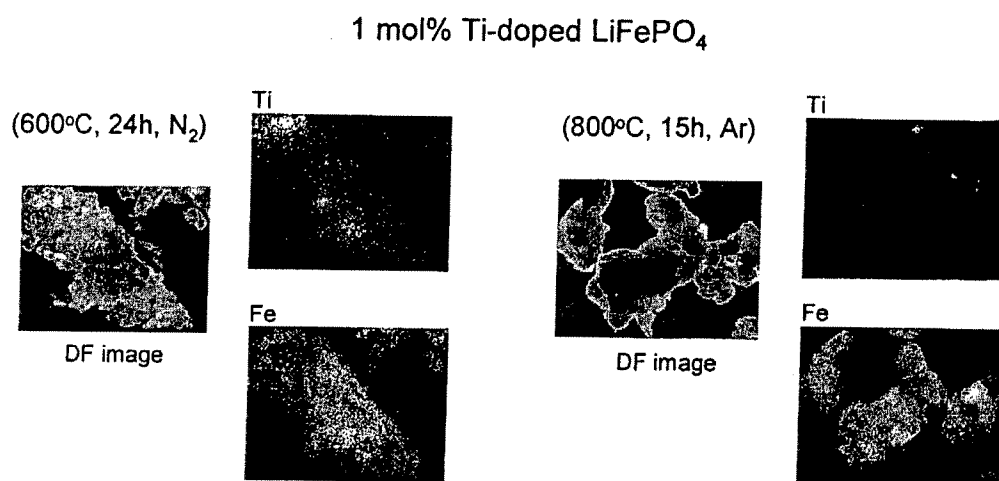


FIG. 3

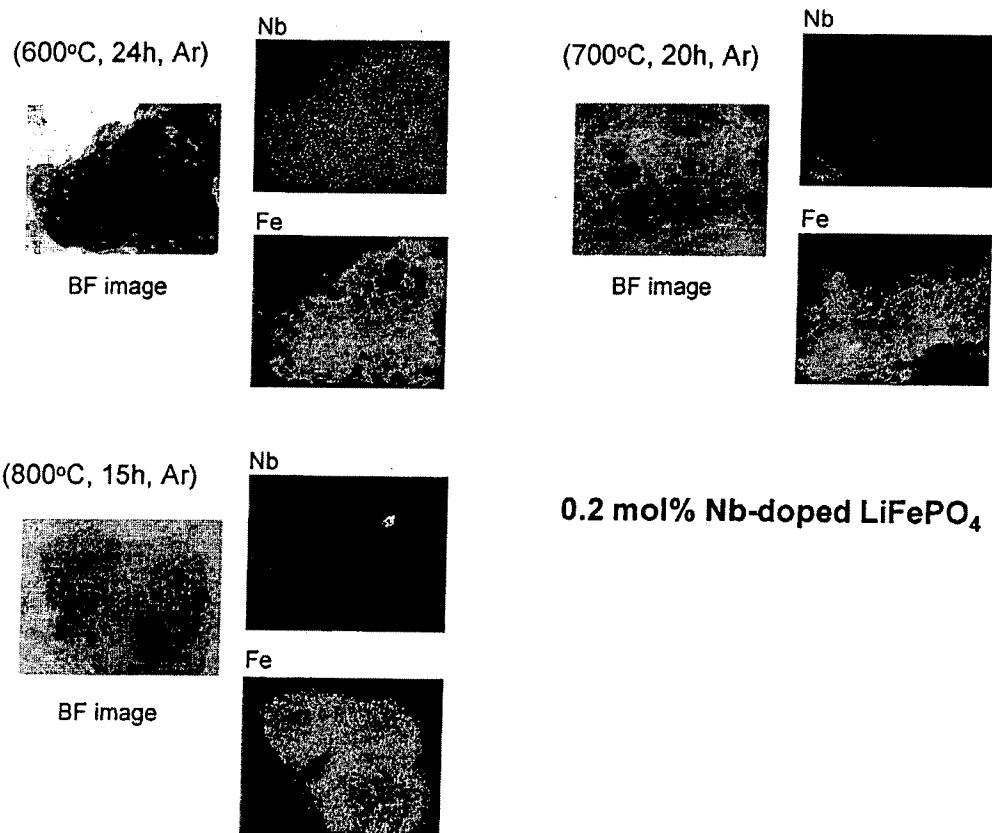


FIG. 4

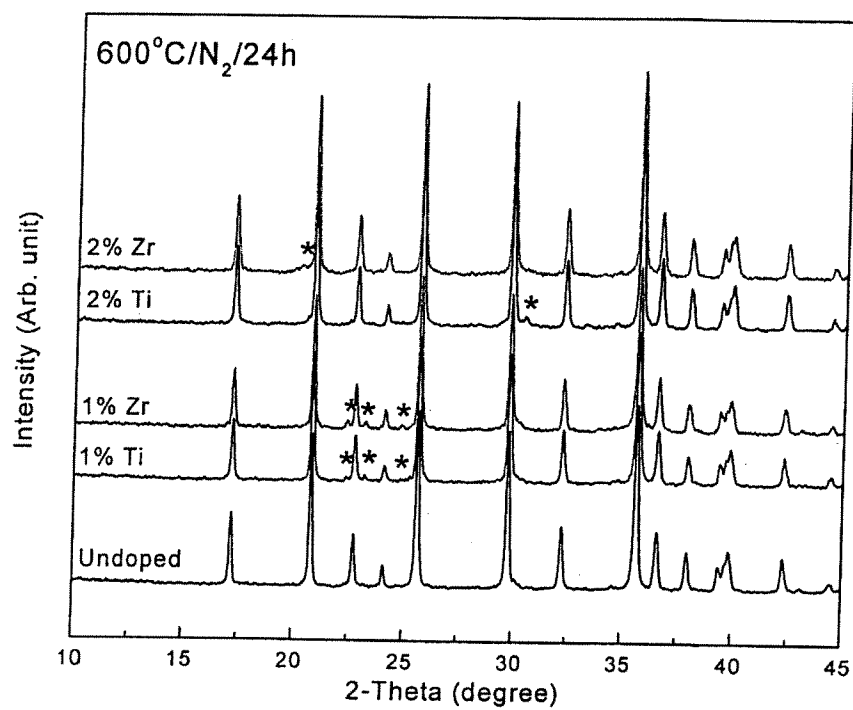


FIG 5.

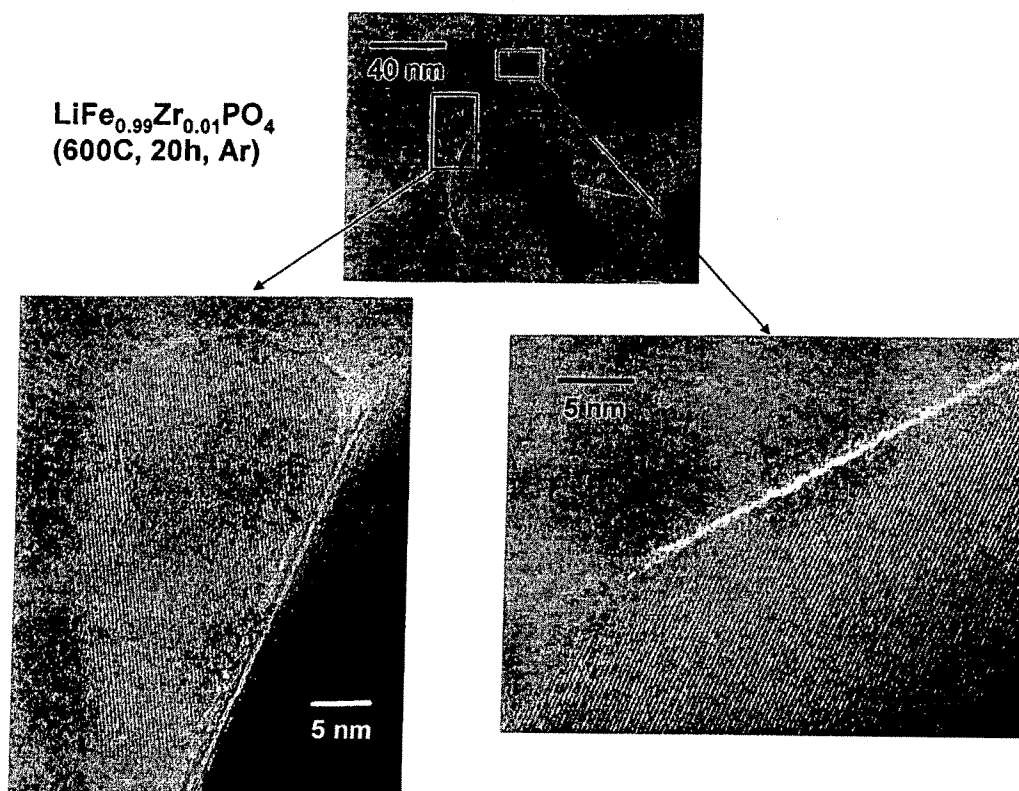


FIG. 6

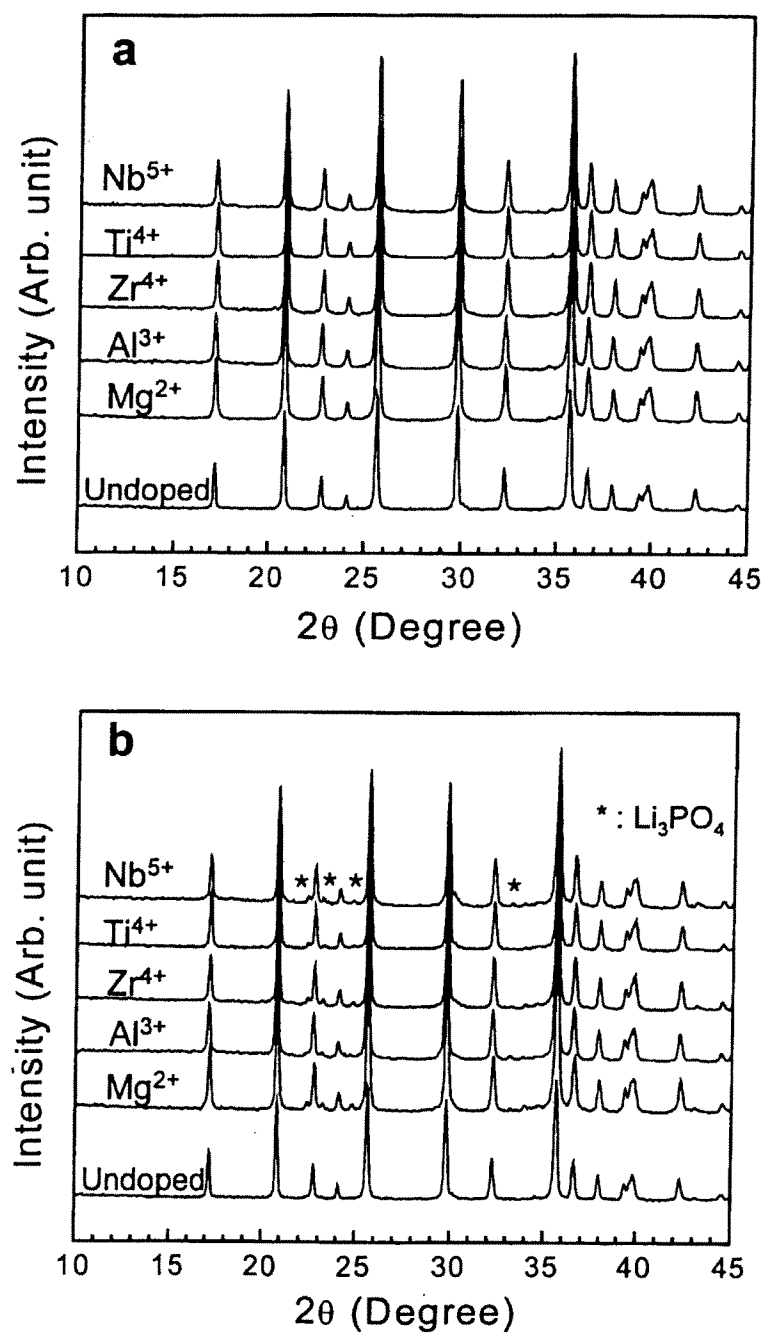


FIG. 7

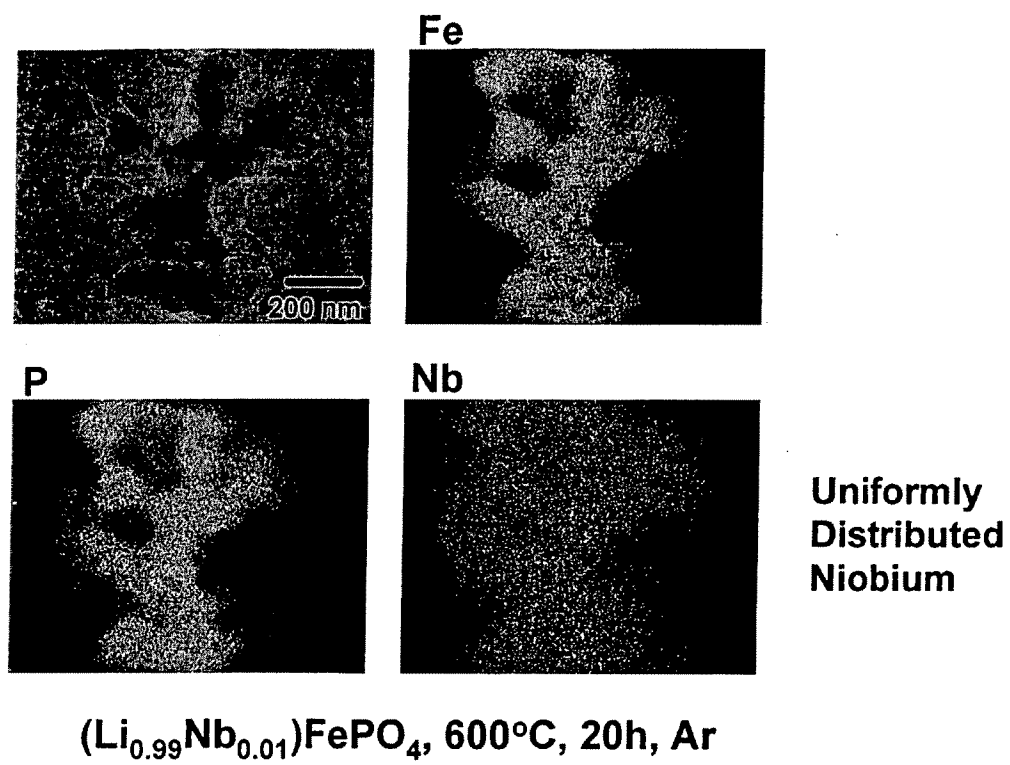


FIG. 8

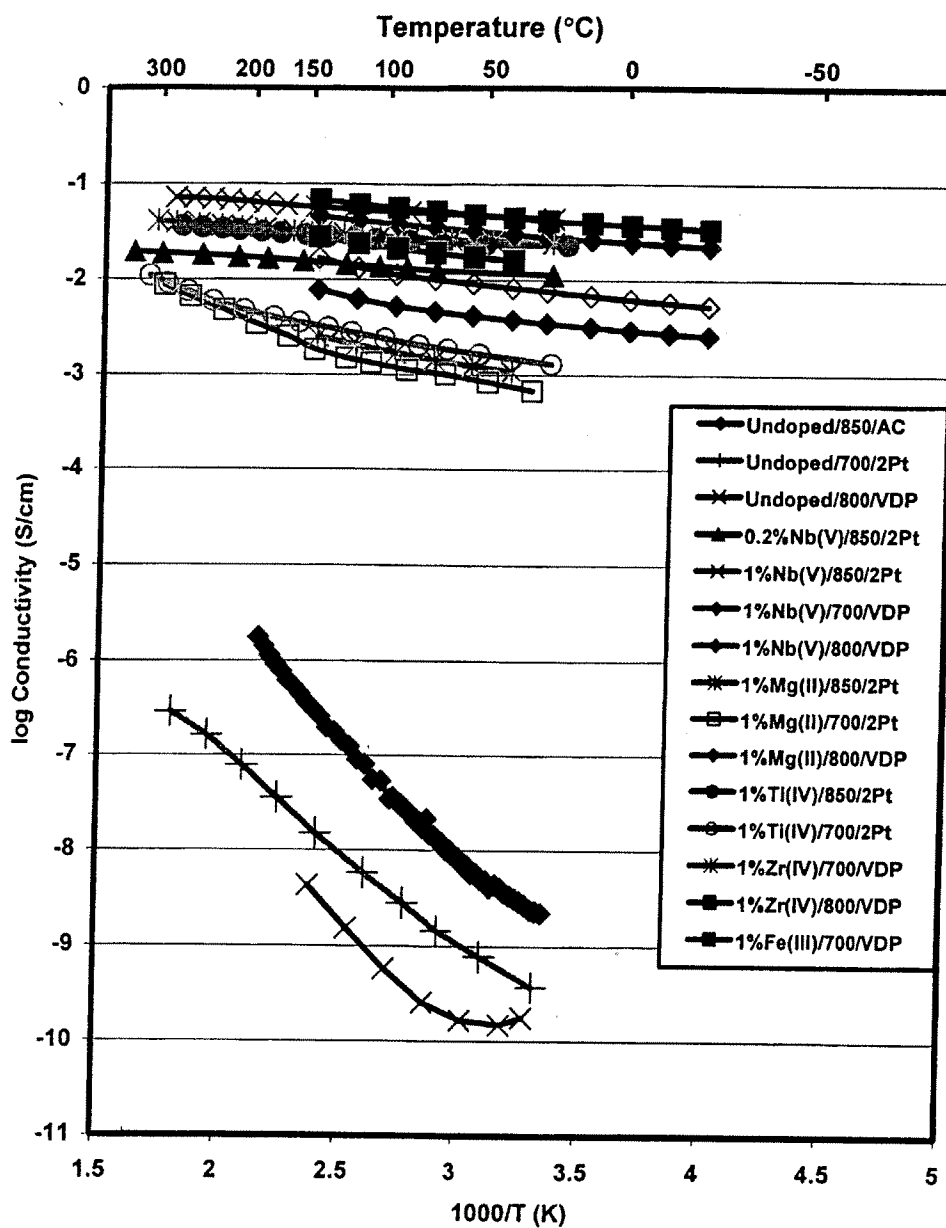


FIG. 9.

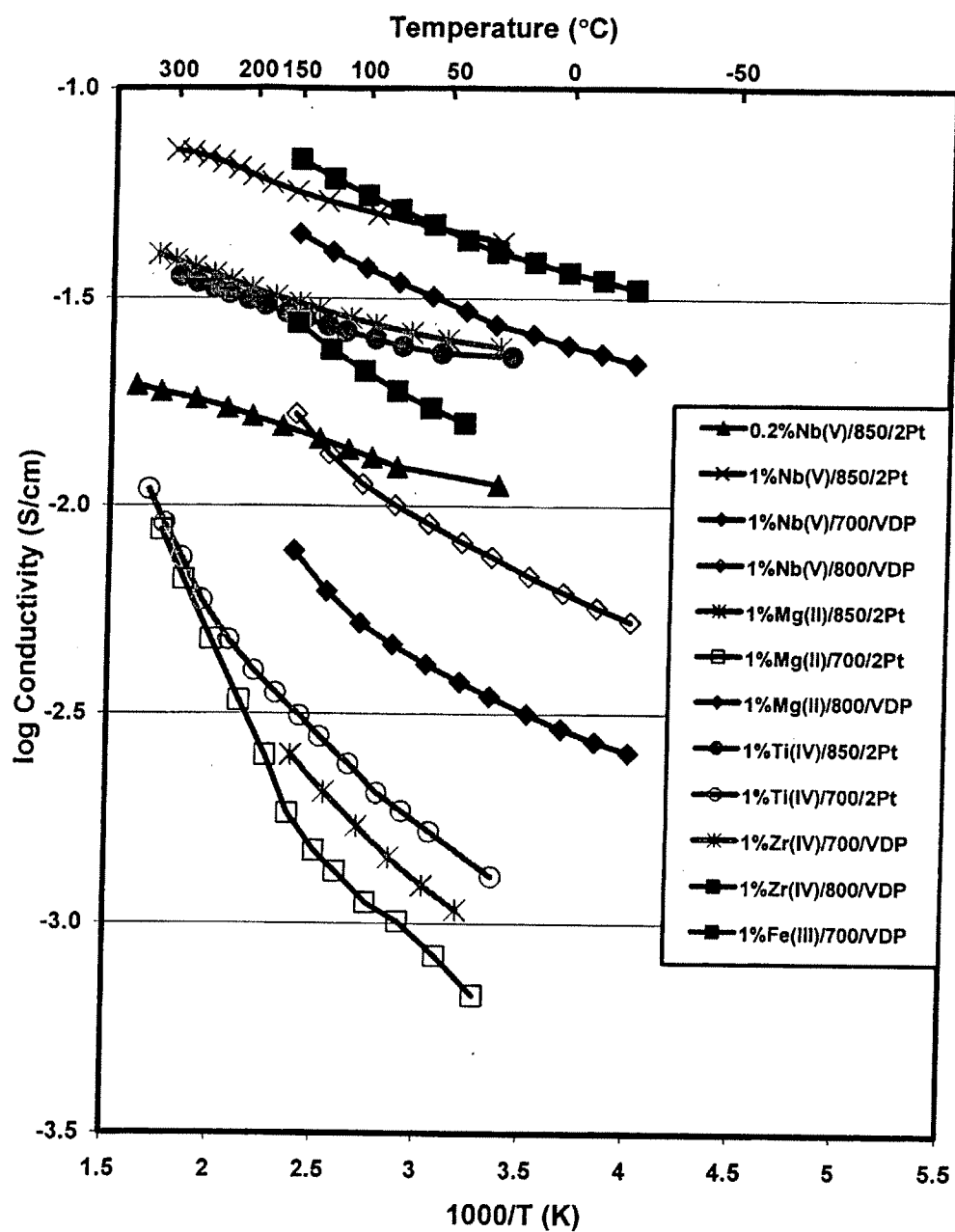
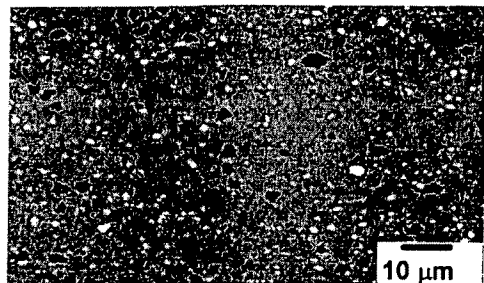
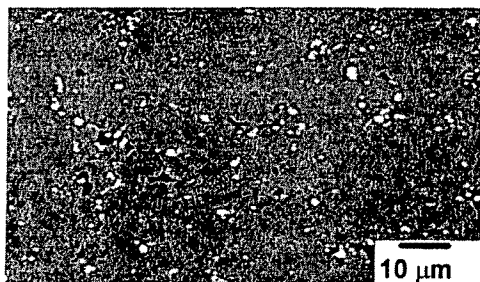


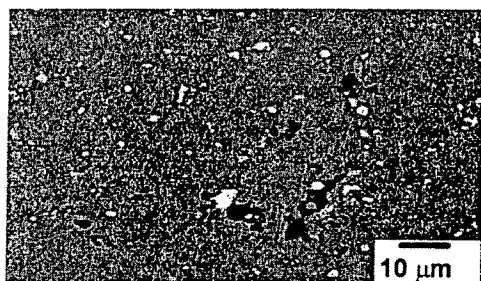
FIG. 10



1% Nb-doped LiFePO_4
Calcined 350°C, sintered 850°C
0.43 wt% carbon



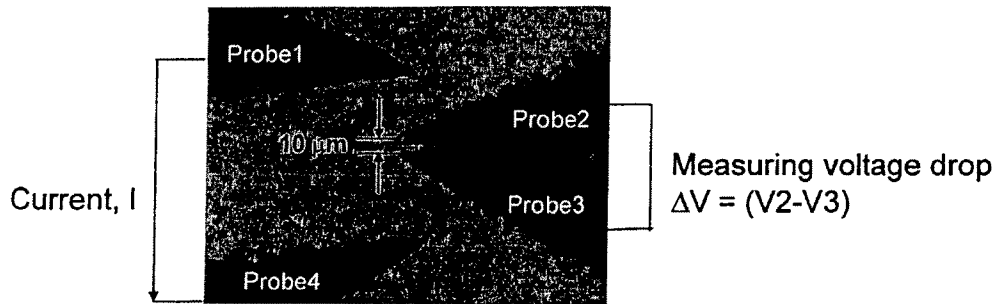
1% Nb-doped LiFePO_4
Calcined 700°C, sintered 900°C
0.22 wt% carbon



Undoped LiFePO_4
Calcined 700°C, sintered 900°C
0.036 wt% carbon

Backscattered electron images

FIG. 11



4-Point Contact Resistivity for Semi-infinite Body¹

$$\rho = 2\pi s R$$

$$R = \Delta V / I$$

s = distance between inner probes ($10\ \mu\text{m}$)

Valid when specimen thickness is $\gg s$

1. L. B. Valdes, Proc. IRE, 42, 420-427 (1954).

FIG. 12

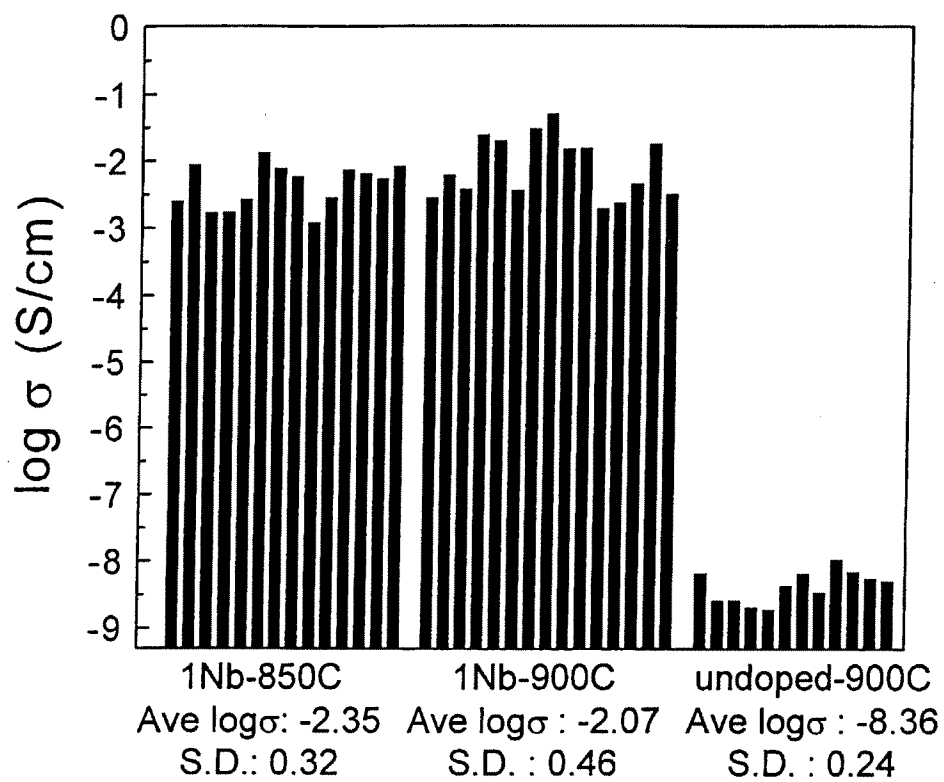
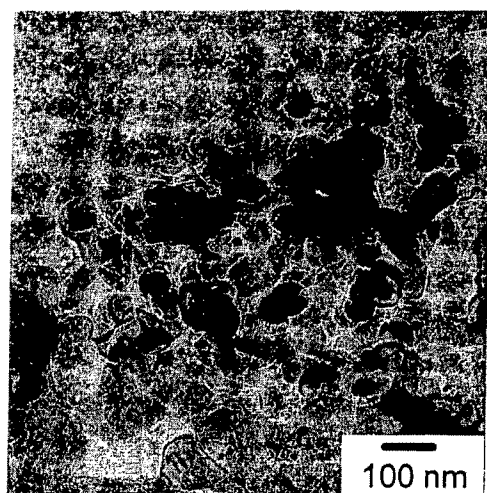
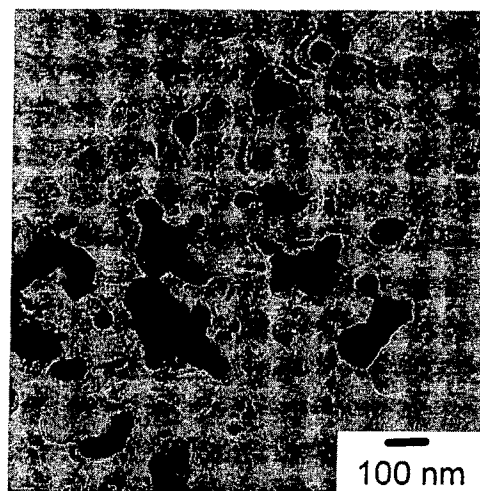


FIG. 13



1 % Nb doped



1 % Zr doped

FIG. 14

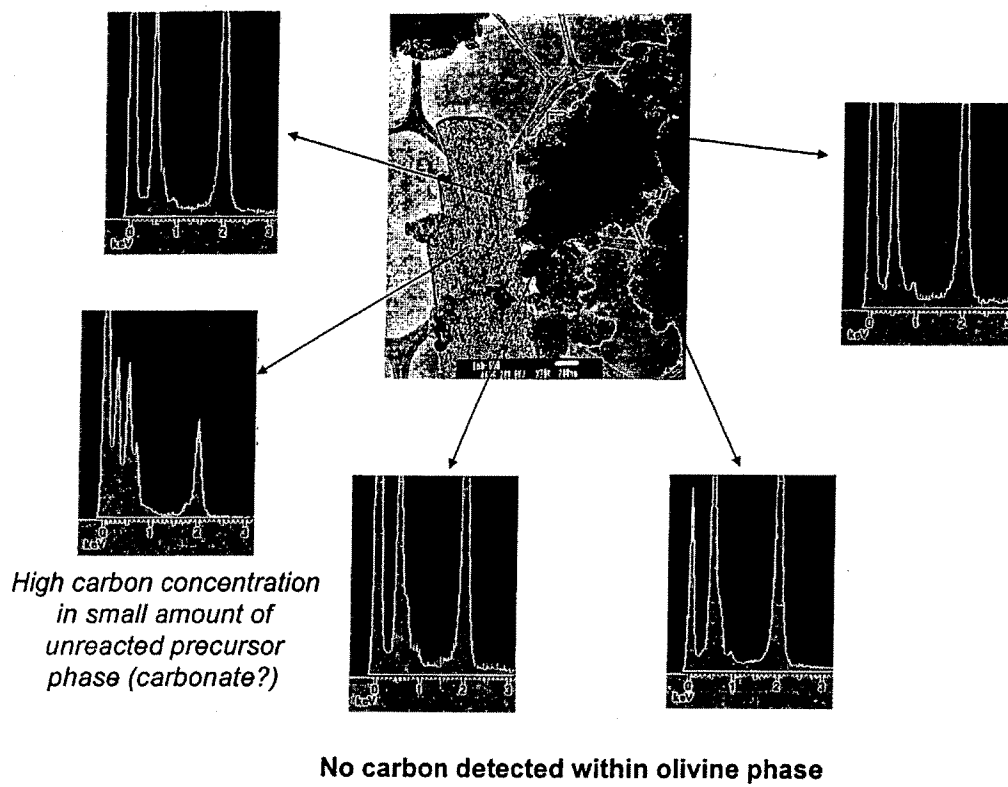
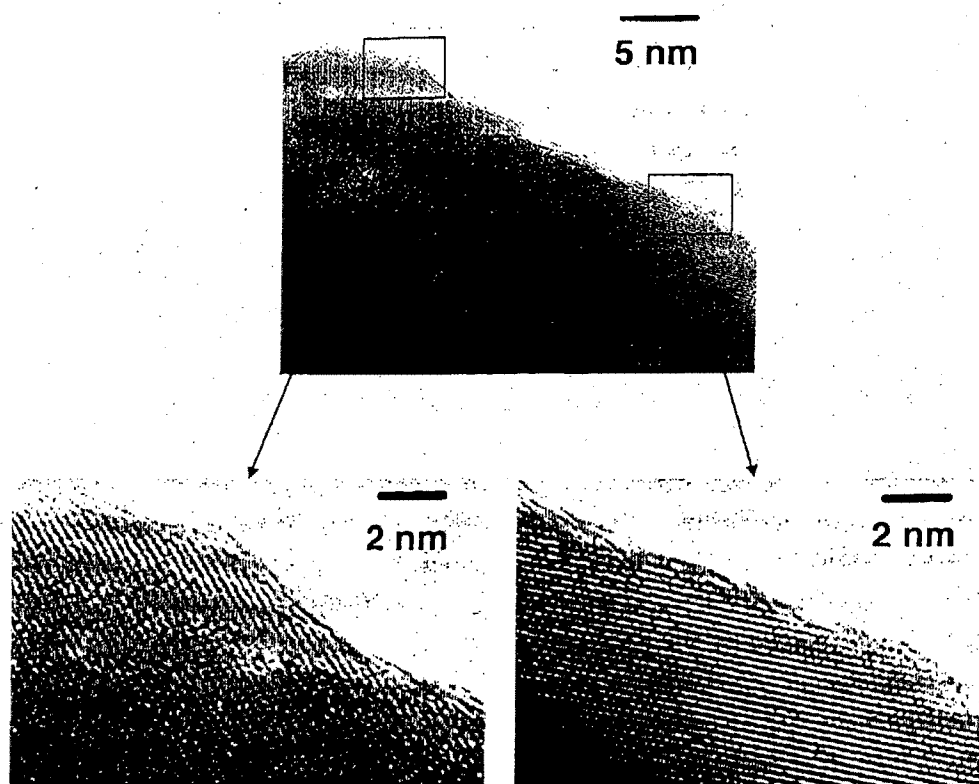


FIG. 16



No surface coating observed

FIG. 15

1% Nb-doped, 600C

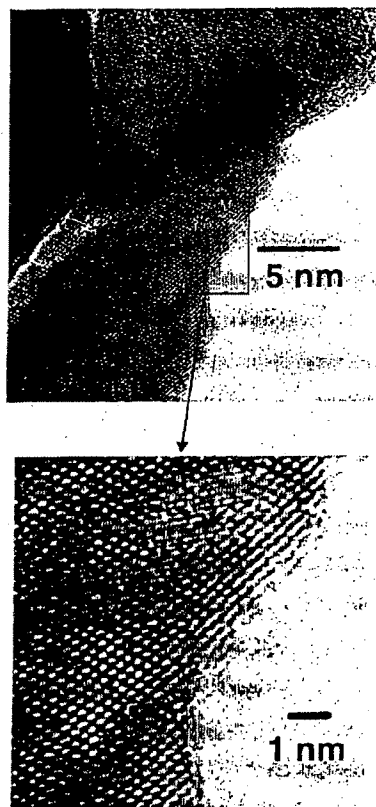
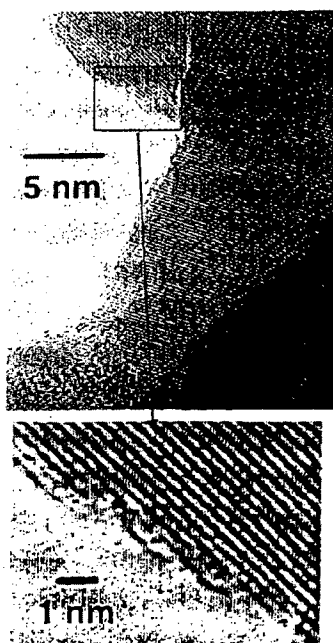
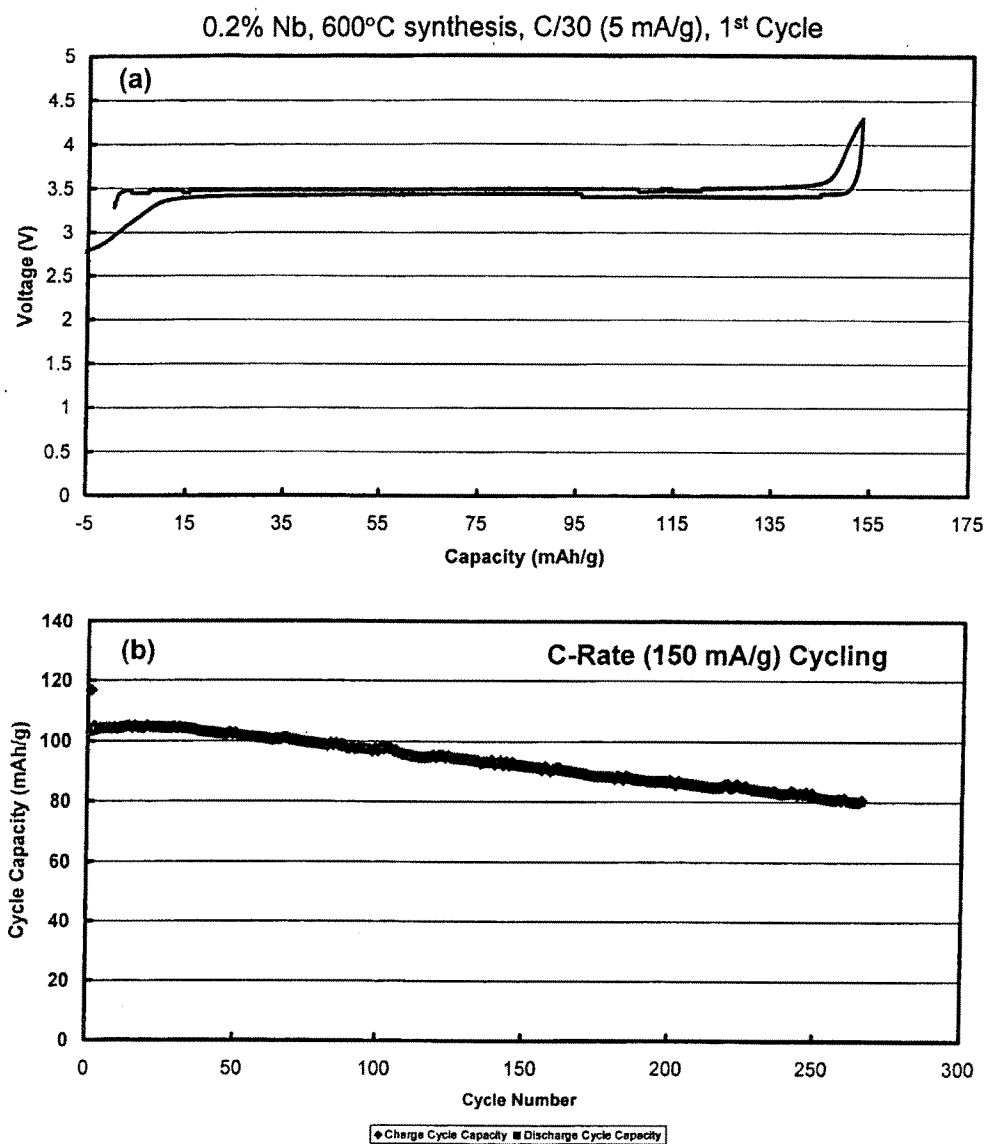
**No surface coating observed**

FIG. 17



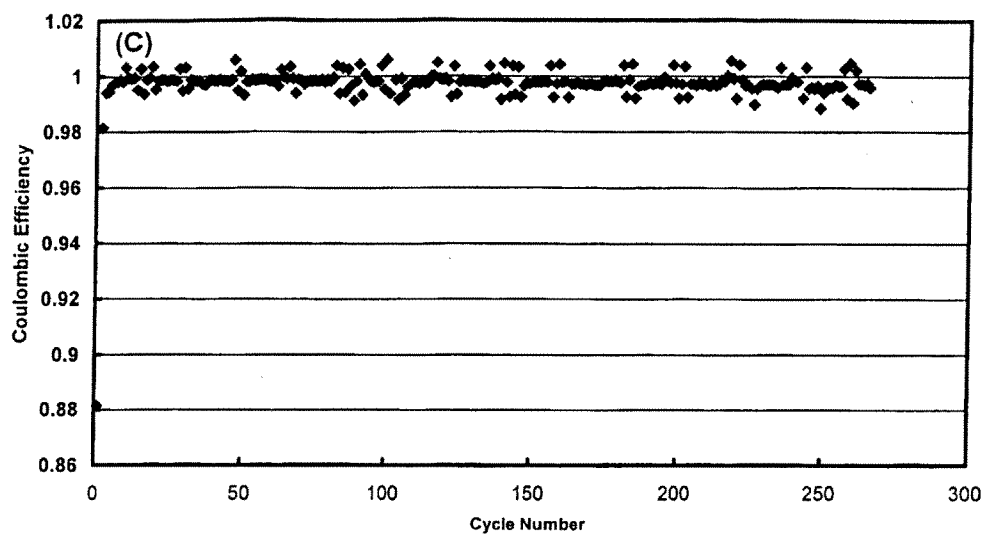


FIG. 18

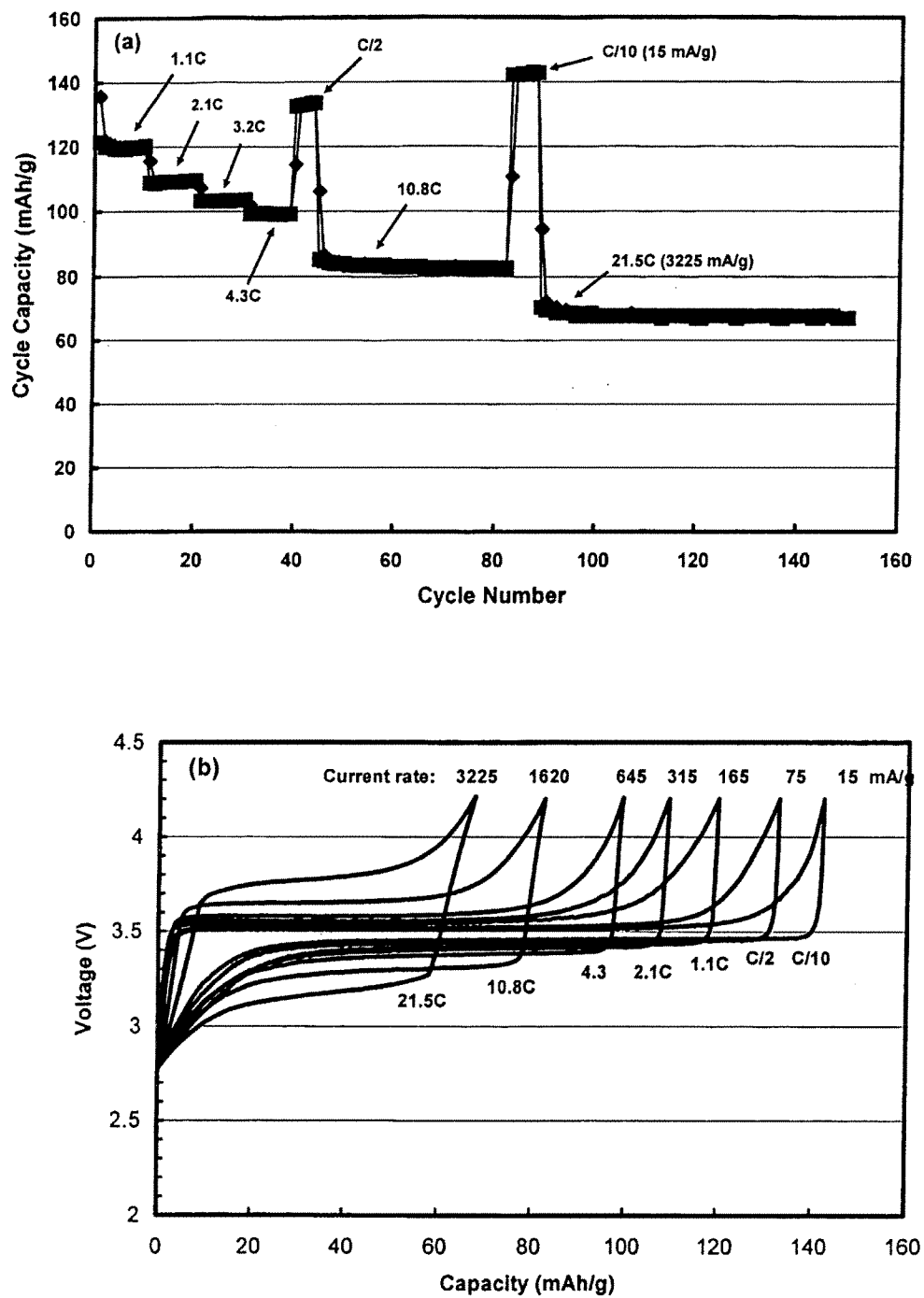


FIG. 19.

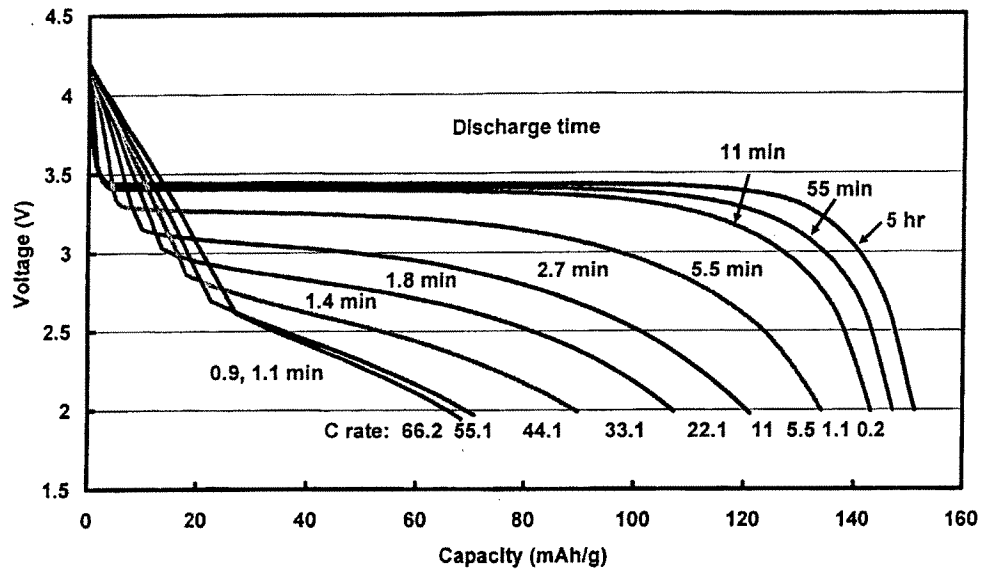


FIG. 20.

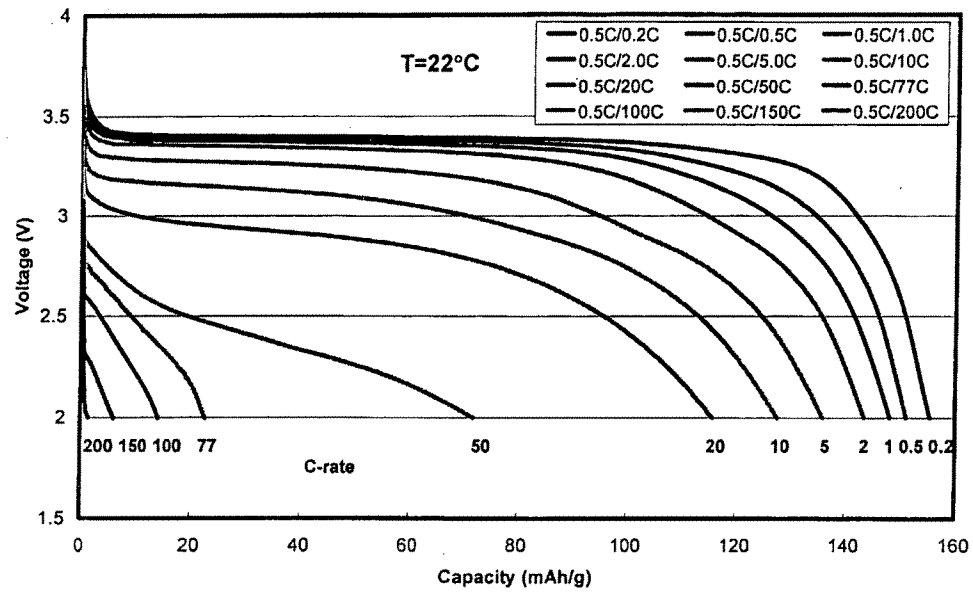


FIG. 21.

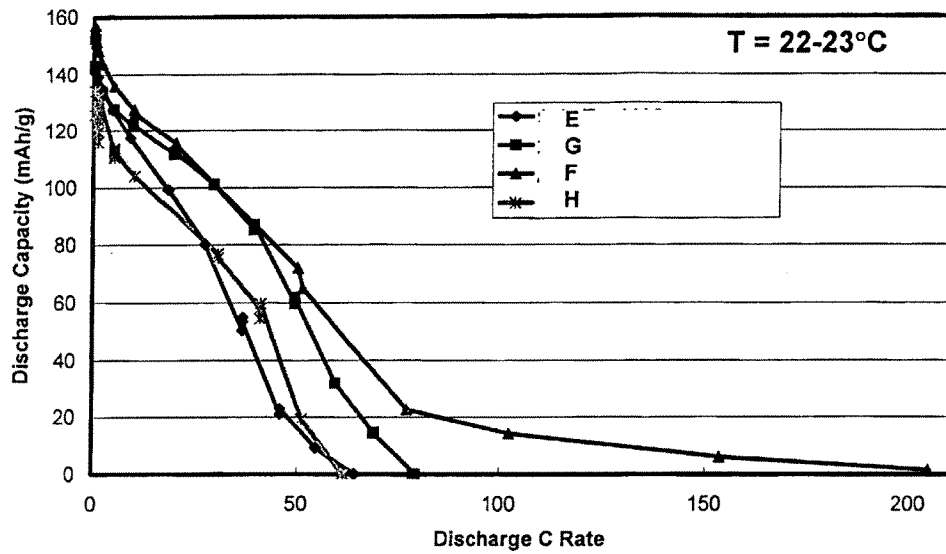


FIG. 22.

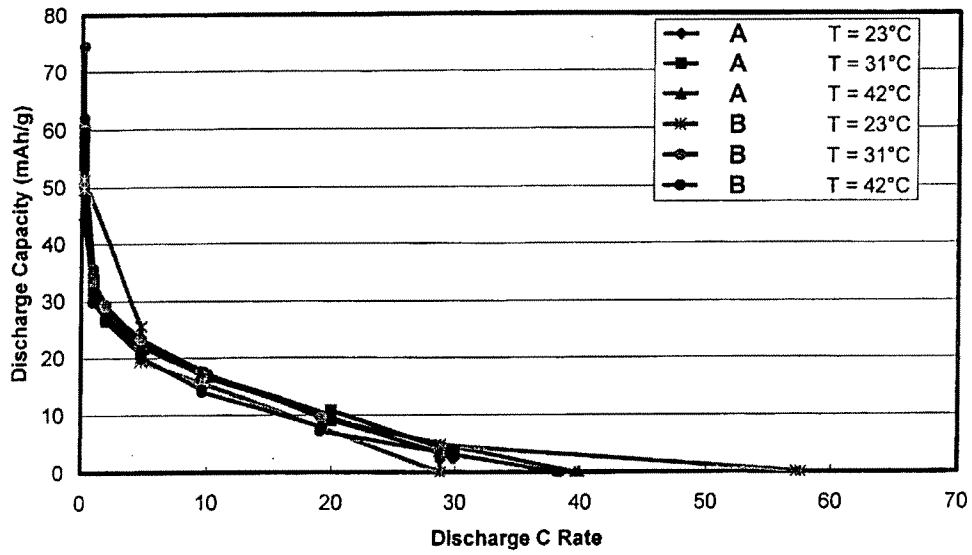


FIG. 23.

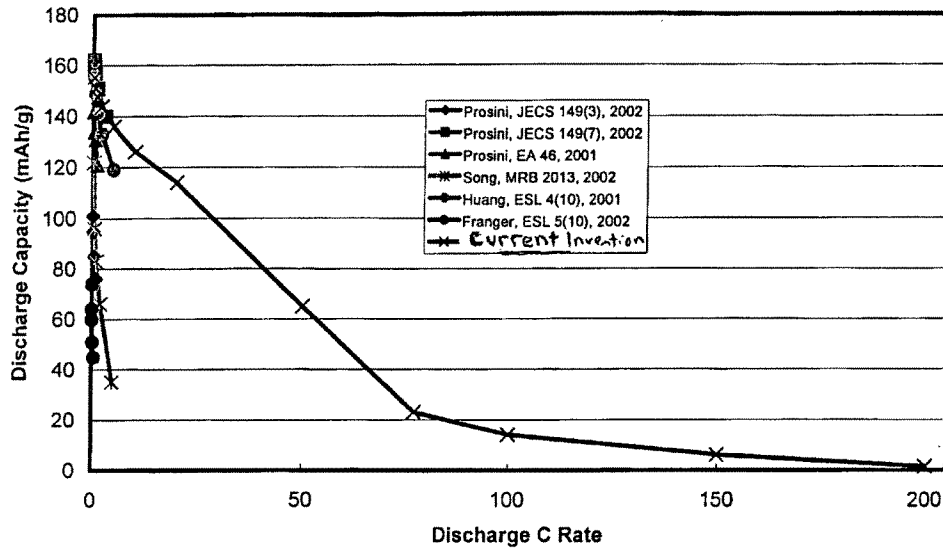


FIG. 24.

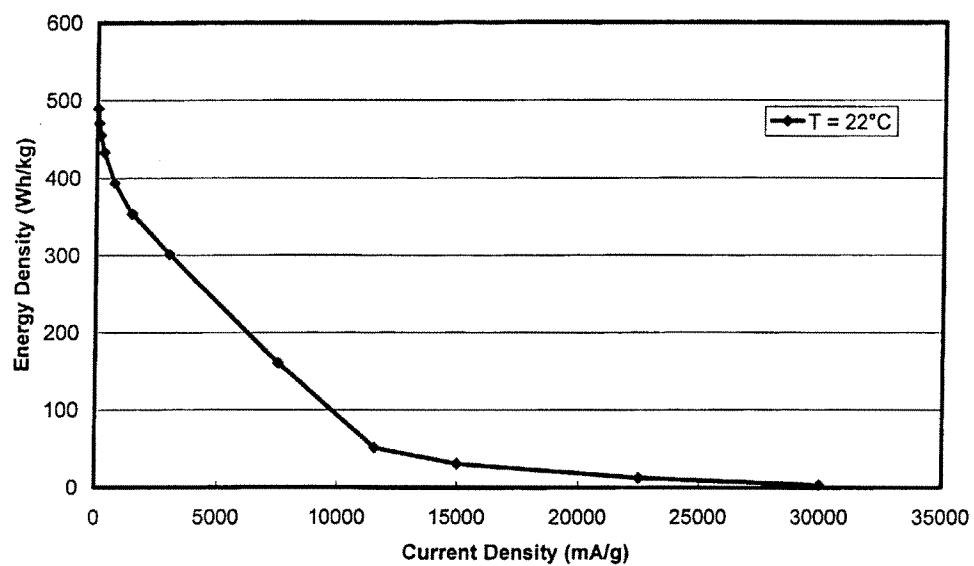


FIG. 25.

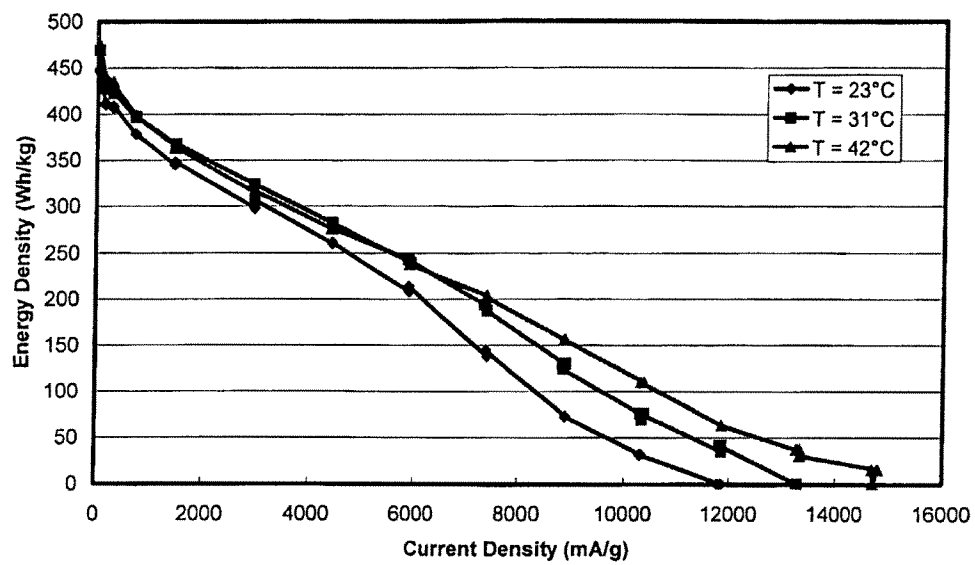


FIG. 26.

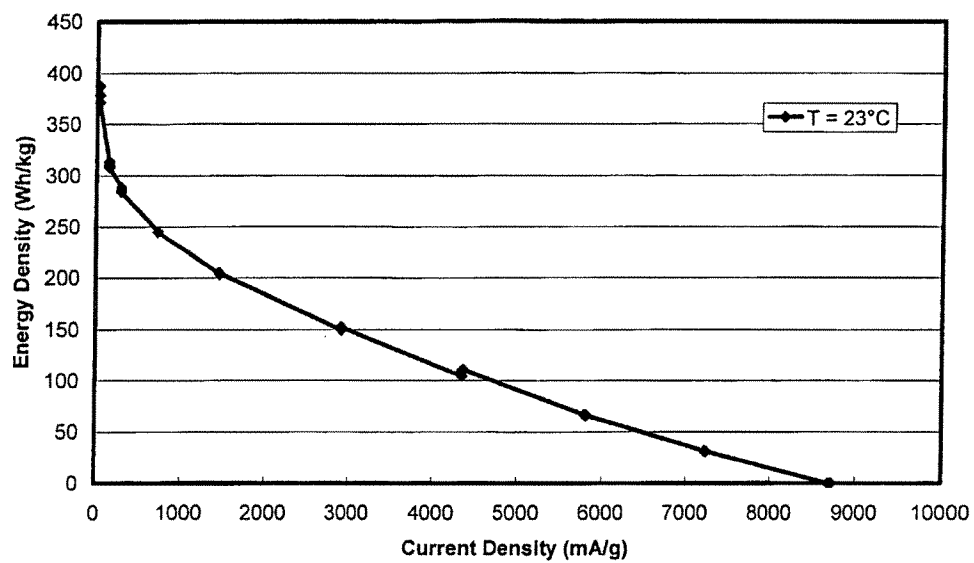


FIG. 27.

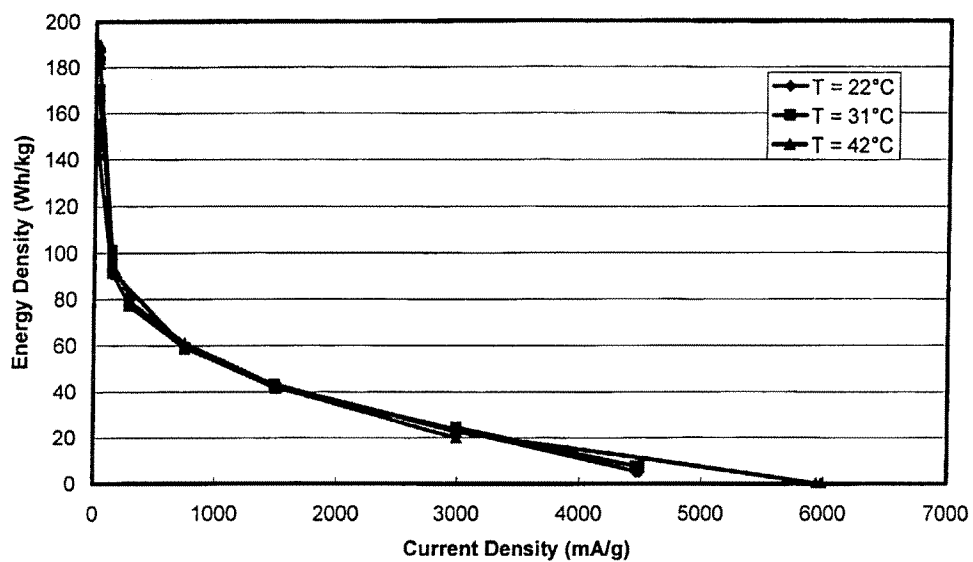
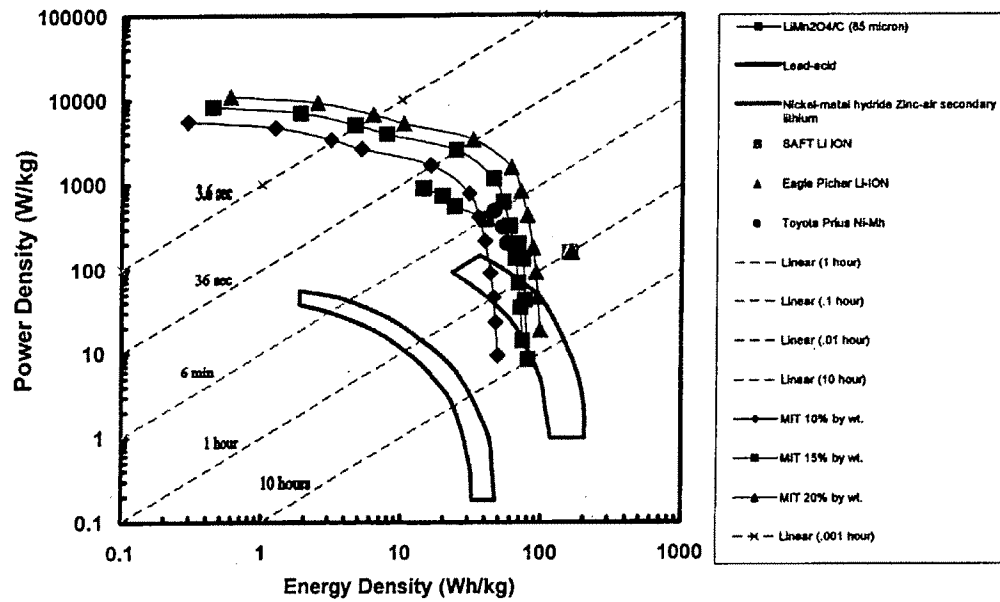


FIG. 28.



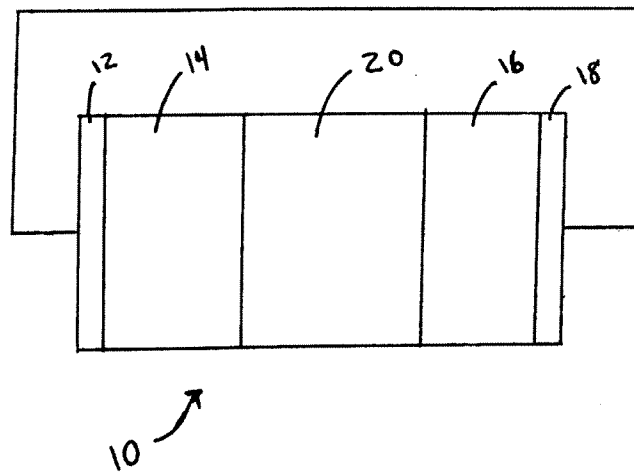


Fig. 29

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 02/41471

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M4/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 933 827 A (MATSUSHITA ELECTRIC IND CO LTD) 4 August 1999 (1999-08-04) paragraph '0035!; claim 13 ---	1-178
X	WO 01 54212 A (BARKER JEREMY ;SAIDI M YAZID (US); VALENCE TECHNOLOGY INC (US)) 26 July 2001 (2001-07-26) claims 1-41; figures 4-10; examples IV-VIII ---	1-178
X	WO 01 53198 A (BARKER JEREMY ;SAIDI M YAZID (US); SWOYER JEFFREY L (US); VALENCE) 26 July 2001 (2001-07-26) claims 1-30; figures 4-10; examples IV--VIII --- -/--	1-178

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

20 March 2003

Date of mailing of the international search report

11/04/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Killian, S

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/41471

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 910 382 A (MASQUELIER CHRISTIAN ET AL) 8 June 1999 (1999-06-08) column 2, line 27 - line 34; claims 1-9; example 1 ---	1-178
X	YAMADA A ET AL: "Crystal chemistry of the olivine-type Li(Mn/sub y/Fe/sub 1-y/)PO/sub 4/ and (Mn/sub y/Fe/sub 1-y/)PO/sub 4/ as possible 4 V cathode materials for lithium batteries" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, AUG. 2001, ELECTROCHEM. SOC, USA, vol. 148, no. 8, pages A960-A967, XP002235417 ISSN: 0013-4651 the whole document ---	1-178
X	RAVET N ET AL: "Electroactivity of natural and synthetic triphylite" JOURNAL OF POWER SOURCES, ELSEVIER SEQUOIA S.A. LAUSANNE, CH, vol. 97-98, July 2001 (2001-07), pages 503-507, XP004254557 ISSN: 0378-7753 table 1 ---	1-178
X	PADHI A K ET AL: "Phospho-olivines as positive-electrode materials for rechargeable lithium batteries" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, ELECTROCHEMICAL SOCIETY. MANCHESTER, NEW HAMPSHIRE, US, vol. 144, no. 4, April 1997 (1997-04), pages 1188-1194, XP002169166 ISSN: 0013-4651 abstract ---	1-178
A	YAMADA A ET AL: "Optimized LiFePO/sub 4/ for lithium battery cathodes" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, MARCH 2001, ELECTROCHEM. SOC, USA, vol. 148, no. 3, pages A224-A229, XP002235418 ISSN: 0013-4651 -----	

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

In view of the large number and also the wording of the claims presently on file, which render it difficult, if not impossible, to determine the matter for which protection is sought, the present application fails to comply with the clarity and conciseness requirements of Article 6 PCT (see also Rule 6.1(a) PCT) to such an extent that a meaningful search is impossible.

Furthermore the claims relate to an extremely large number of possible compounds, products, apparatus and methods. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds, products, apparatus and methods claimed.

In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible.

Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compounds, products, apparatus and methods recited in the Tables 2, 4 and 5, i.e. relating to LiFePO_4 doped with Al, Ti, Zr, Nb, Ta, W, Mg, Mn^{2+} , Fe^{2+} and Li.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 02/41471

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/41471

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0933827	A	04-08-1999	JP 11219722 A	10-08-1999
			EP 0933827 A1	04-08-1999
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			US 2002086214 A1	04-07-2002
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			EP 0904607 A1	31-03-1999
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			WO 9740541 A1	30-10-1997